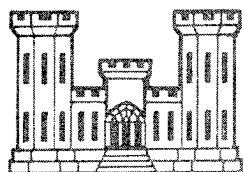


**DISTRIBUTION OF  
SELECTED TRACE ELEMENTS  
IN ROCKS**

**RONALD J. KLEY**

**February 27, 1968**



**U.S. ARMY ENGINEERS  
Nuclear Cratering Group  
Livermore, California**

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PNE-5008

Distribution of Selected  
Trace Elements in Rocks

Ronald J. Kley

U. S. Army Engineer  
Nuclear Cratering Group  
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# DISTRIBUTION OF SELECTED TRACE ELEMENTS IN ROCKS

## Abstract

This report discusses factors influencing trace element distribution in rocks, tabulates maximum and minimum concentrations of twenty-nine trace elements in various common rock types, and briefly describes the geochemical behavior of each of these elements. A procedure is outlined for predicting concentrations of these selected elements in various rock types.

On the basis of this study it is concluded that:

1. Trace element concentration varies systematically according to the gross mineralogical composition of the host rock.
2. Mineralogical composition of the host rock is the primary determinant of trace element concentrations.
3. Knowledge of rock mineralogy as provided by conventional petrographic analyses serves as a basis for estimating trace element concentrations.

## Introduction

The purpose of this report is to determine the concentrations of certain trace elements\* in common rock types, and to provide a basis for predicting trace element concentrations in geological media.

An accurate knowledge of the chemical composition of the geological medium is required when the radiological hazards of a nuclear cratering event are to be evaluated (e. g., in predicting the biological effects of radionuclides produced by a nuclear cratering event). Trace elements are of

particular significance in such an evaluation, because: (1) this group includes some elements whose radionuclides, in large enough concentrations, could result in body burdens of potential danger to man, and (2) these elements are not ordinarily detected in routine petrographic or chemical analyses.

The estimation of specific activities for trace element radionuclides, therefore, is of significance in:

1. Studies to determine the feasibility of using nuclear explosives in large excavation projects.
2. Site selection for and design of nuclear cratering experiments.

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\*Those elements (also known as "minor" or "accessory" elements) whose concentrations in common rocks are usually less than 1000 ppm.

3. Development of experimental programs to determine possible levels and loci of concentration, in the biosphere, for various radionuclides which might be produced in the course of a proposed nuclear excavation project.

This paper, in providing an improved method for predicting the concentrations of trace elements in various rock types, supports the Feasibility Study Program of the U. S. Army Corps of Engineers Nuclear Cratering Group. The improved capability will (1) facilitate calculation of specific activities for radionuclides resulting from nuclear cratering events, and (2) permit a more accurate estimate of the potential long-term radiation dose to man resulting from radionuclides produced and distributed by underground nuclear detonations.

The data in this report, together with data regarding concentrations of the same elements in nuclear device components, may be used to calculate the specific activities of radionuclide counterparts produced from these elements during initial cavity formation. These specific activities may then be directly compared to permissible specific activities for radionuclide intake in man. Such a comparison serves as a convenient means for

identifying those radionuclides whose concentrations may be great enough to warrant more detailed consideration.

The data in this report supplement those presented for 15 other trace elements in PNE-5006.<sup>1</sup> Unlike PNE-5006, this report deals only with trace element concentrations in various rock types, and does not consider the problem of calculating neutron-induced radioactivity as a function of elemental concentrations. The methods for such calculations as described in PNE-5006, however, are also valid for the elements considered in this report.

This report is based upon an extensive review of published geochemical literature and a tabulation of the quantitative data which was obtained. The theoretical and descriptive data presented in this report are based upon such standard textbooks of geochemistry as Rankama and Sahama,<sup>2</sup> Mason,<sup>3</sup> and Goldschmidt.<sup>4</sup> Additional empirical data were obtained from the literature of mining geology—particularly from such standard reference texts as Lindgren,<sup>5</sup> Bateman,<sup>6</sup> McKinstry,<sup>7</sup> and Gillson.<sup>8</sup> Raw analytical data were obtained primarily from journals devoted to geochemical research, such as Geochemistry and Geochimica et Cosmochimica Acta.

## Factors Governing Trace Element Distribution

### BACKGROUND

The available empirical, analytical, and theoretical data indicate that the distribution of chemical elements (and particularly that of trace elements) in rock depends upon two major variables:

1. The availability of various elements at the time and place of rock formation.
2. The affinity of the particular rock for various elements.

Variations of trace element availability from place to place and from time to time have been demonstrated and described in

detail. Stoiber<sup>9</sup> has shown that the variation of trace element concentrations with respect to time and place is systematic, and that minerals formed at a given time and within a given district are likely to exhibit both a qualitative uniformity of trace element content and a consistently high or low concentration of each trace element. More recently, Burnham<sup>10</sup> has presented corroborative empirical evidence. There is as yet, however, no adequate basis for explaining or predicting these variations.

The mutual affinities of certain trace elements and certain rocks, on the other hand, can be largely accounted for on the basis of well-established physical and chemical principles. These principles, therefore, may provide a logical basis for estimating trace element concentrations in rock and predicting induced radioactivity from nuclear detonations in various geological media.

#### EFFECT OF MINERALOGY ON TRACE ELEMENT DISTRIBUTION

Chemical analyses and other geochemical data frequently convey the impression that rocks consist of homogeneous matter in which elemental constituents are distributed at random. In fact, however, rocks are generally composed of several different minerals which differ from one another both physically and chemically. Rock-forming minerals are crystalline solids made up of specific atomic units arranged in specific three-dimensional arrays or lattices. If any trace element is to be found in a rock, therefore, it must generally be present as an integral component of the lattice structure in one or more of the rock-forming minerals.

With relatively few exceptions,\* the occurrence of a trace element in a rock-forming mineral is dependent upon the ability of the trace atom or ion to substitute for one of the more abundant elements which comprise the essential stoichiometric constituents of the mineral. The extent of such atom-for-atom or ion-for-ion substitution (or diadochy) is proportional to the degree of similarity (with respect to atomic or ionic radii, electrostatic charge or valence, and bonding characteristics) between the proxy and proxied-for units.

The following illustration, though somewhat oversimplified, offers an example of a chemical-mineralogical relationship and the predictive inferences which may be drawn from it:

1. The element rubidium is not an essential stoichiometric constituent of any known mineral. Because of its chemical similarity to potassium however, it is able to proxy for this more abundant element in

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\*Trace elements may also occur (a) as stoichiometric components of certain rare minerals, (b) as superficially adsorbed atoms or ions, (c) as anomalous inclusions occupying structural defect positions or interstices between regular structural positions, or (d) as constituents of intragranular fluid inclusions. Type "a", "b", and "c" occurrences are, like diadochic substitution, dependent upon host rock mineralogy. Fluid inclusions which provide the loci for type "d" occurrences generally comprise so small a portion of total rock volume as to be of no significance with respect to overall rock composition. Moreover, because the contents of such inclusions presumably represent a fluid phase which was in chemical equilibrium with coexisting solid phases at the time of rock formation, it is unlikely that a marked qualitative or quantitative disparity would exist between the trace element content of the fluid and that of the enclosing rock.

a number of common rock-forming minerals, e.g.:

orthoclase  $\text{KAlSi}_3\text{O}_8$

muscovite  $\text{KAl}_3\text{Si}_3\text{O}_{10}$

biotite  $\text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$

nepheline  $(\text{K}, \text{Na})(\text{Al}, \text{Si})_2\text{O}_4$

Thus, by determining the relative concentrations of these readily identifiable potassium-bearing minerals in various rocks, it is possible to estimate the relative rubidium concentrations to be expected in these rock types.

2. As shown in Fig. 1, the more "basic" igneous rocks such as peridotite and gabbro are essentially devoid of potassic minerals. In passing from these basic rocks through those of "intermediate" composition, such as diorite and granodiorite, to the more "acidic" varieties, including granite and syenite, the total percentage of potassic

minerals increases steadily. One might predict on this basis that rubidium would be primarily concentrated in the acidic igneous rocks, be present (but in substantially lower concentrations) in the intermediate varieties, and be present only sparingly, if at all, in the basic rocks. (This prediction is in close accord with the available analytical data in Table I.)

3. It is not possible to draw a similarly straightforward diagram to illustrate compositional variations among sedimentary and metamorphic rocks, because their nomenclature is based largely upon texture, structure, and grain size rather than upon their mineralogical composition. The distribution of rubidium in these rocks can, however, be accounted for on the basis of equally elementary geological considerations.

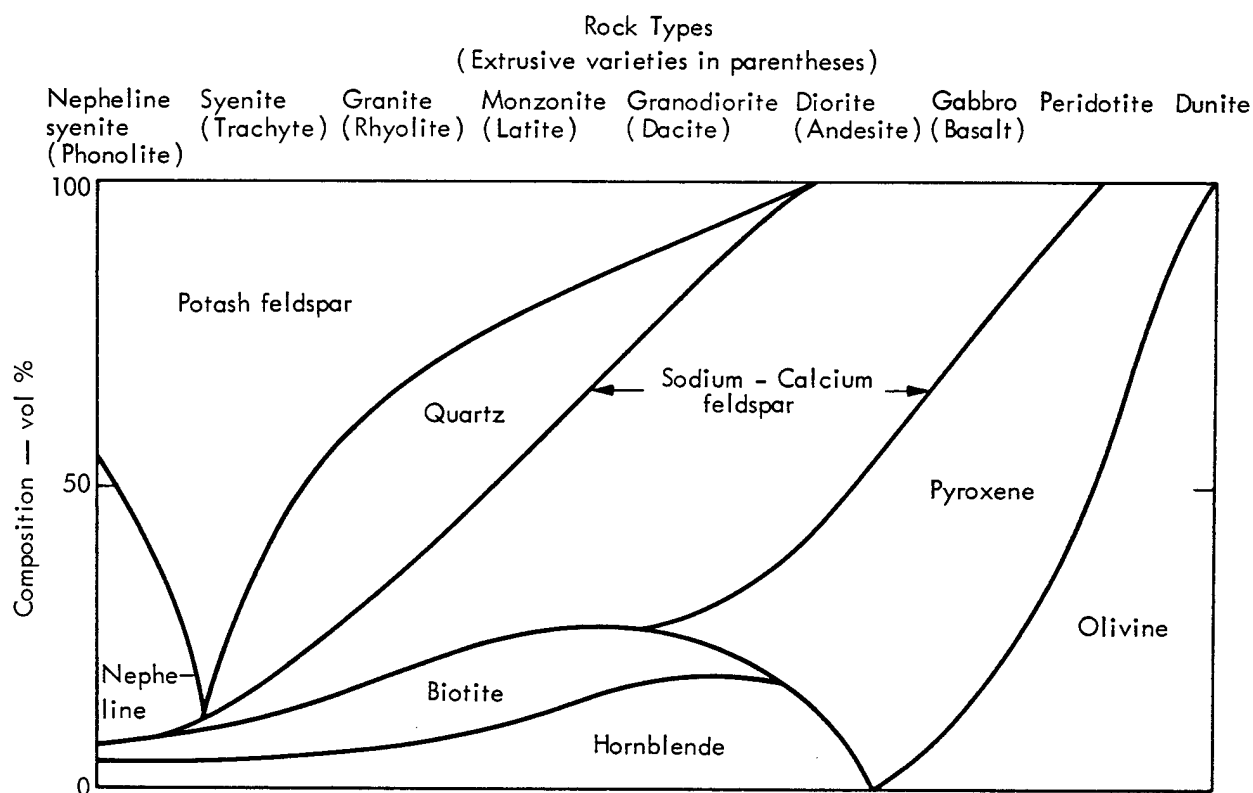


Fig. 1. Gross mineralogical composition of some common igneous rocks. (Adapted from Mason.<sup>3)</sup>)

Orthoclase, which is generally the most abundant potassic mineral in igneous rocks, decomposes under conditions of extended weathering, with its potassium (and presumably any associated rubidium) being carried away in solution or adsorbed by clay minerals. Thus a sedimentary rock such as sandstone, composed of those rock and mineral fragments which have resisted the weathering of the older rock from which they were derived, will contain few potassic minerals and correspondingly little rubidium. Similarly, pure limestone, composed entirely of calcium carbonate, has no mineralogical affinity for the rubidium ion; though impurities which are present in many limestones may be responsible for some anomalously high concentrations. Shales and other pelitic sediments, on the other hand, contain a substantial percentage of clay minerals (illite and montmorillonite in particular), which are capable of including or adsorbing appreciable quantities of potassium. These rocks, therefore, are often found to be enriched in rubidium.

4. Metamorphic rocks, formed by the recrystallization of pre-existing rocks with little or no addition or subtraction of chemical constituents, show trace element concentrations similar to those of the pre-existing rock. Slates, phyllites, and schists which have been derived from shales or other pelitic sediments, therefore, are predictably rich in potassium and associated rubidium. Quartzites and marbles, the metamorphic equivalents of sandstones and limestones, respectively, contain relatively little potassium or rubidium. "Greenstones" and dark colored gneisses, derived from basic igneous rocks, usually have low potassium

and rubidium concentrations. Light colored gneisses derived from acidic igneous rocks generally show a significant concentration of both potassium and rubidium.

#### EFFECT OF MUTUAL INTERACTION ON TRACE ELEMENT DISTRIBUTION

As discussed in the preceding section, the structural sites available to a trace element in a rock are rigorously defined by the mineralogy of that rock. When several trace elements are competing for structural sites within the same minerals (as would usually be the case in any petrogenetic environment), extremely complex multiple substitution and mutual interaction may develop.

There is a paucity of data concerning the interaction of two or more trace elements which are potential proxies for the same structural sites. It has been suggested by Goldschmidt,<sup>4</sup> however, on the basis of empirical and theoretical evidence, that:

1. If two or more potential proxies are present in the geochemical environment, the one most similar (with respect to ionic radius and charge) to the proxied-for cation will be preferentially incorporated into the crystal structure of the host mineral.
2. If two or more potential proxies have similar ionic radii but dissimilar charges, the one with the higher ionic charge will be preferentially incorporated into the host mineral.
3. If two or more potential proxies have similar charges but dissimilar ionic radii, the one with the smaller ionic radius will be preferentially incorporated into the host mineral.



4. If two or more potential proxies, similar in other respects, develop chemical bonds in coordination with oxygen which differ in degree of covalency, the one whose bonding characteristics most closely approximate those of the proxied-for cation will be preferentially incorporated into the host mineral.

Even fewer data are available concerning possible interactions between two or more elements which are potential proxies for different structural positions within a given crystal lattice. The incorporation of any atomic or ionic impurity into the lattice of an otherwise stoichiometric mineral will produce certain structural stresses due to the dissimilarity, however slight, between the size, electrovalency, or bonding characteristics of the proxy and proxied-for units. The entry of additional proxy units into other lattice positions, therefore, is governed (or at least influenced) by the degree to which such further substitutions accentuate or compensate for the structural stresses imposed by the initial incorporation of proxy units.

#### TRACE ELEMENT DISTRIBUTION AND GEOTHERMOMETRY

In general, the tolerance of a crystal lattice to structural imperfection is proportional to temperature. Thus, other factors being equal, crystals of a given mineral formed at high temperatures will be able to incorporate greater quantities of a trace element than crystals of the same mineral which have formed at lower temperatures. Attempts are being made<sup>11,12,13</sup> to make use of such temperature-dependent trace element variations as geothermometers. To the

extent that these efforts are successful it should be possible to employ other geothermometric criteria (e.g., phase equilibria) to obtain approximations of trace element concentrations.

A major drawback to this approach, however, is that "other factors being equal" is a condition which is seldom fulfilled in nature. Many factors, including pressure, Eh, pH, the nature and proportions of co-existing mineral phases, and both the relative and absolute abundances of all trace elements in the geochemical environment, may have an effect upon the amount of a given element incorporated in a specific mineral at any given temperature and it is seldom possible to evaluate either the relative influence of these various factors or the specific effects of any one of them.

The possibility also exists that solid-state reactions over the span of geologic time will result in a redistribution of trace elements to achieve a condition of low-temperature equilibrium which may differ markedly from that established during initial crystallization. Perhaps the best known example of such a transformation is the development of perthitic feldspar (an intimate intergrowth of albite— $\text{NaAlSi}_3\text{O}_8$ , and orthoclase— $\text{KAlSi}_3\text{O}_8$ ) by exsolution of albite from the orthoclase crystal structure. To the extent that a sizeable mass of rock represents a closed chemical system, however, such transformations would not invalidate estimates of whole-rock trace element concentrations based upon geothermometry.

#### TRACE ELEMENT CONCENTRATIONS AND PHYSICAL PROPERTIES OF MINERALS

Because interatomic or interionic distances, bond strengths, and bond types

are vectorially anisotropic within the crystal structures of rock-forming minerals, proxy structural units are preferentially incorporated in those positions (i.e., on those crystallographic growth planes) where the structurally significant properties of the proxy element most closely approximate those of the proxied-for atoms or ions. Such preferential concentrations of proxy units may increase or decrease the relative growth rates in different crystallographic directions; and such vectorial contrasts in crystal growth rates will, in turn, control the morphology of a crystal (because degree of development of any given crystallographic plane is inversely proportional to the rate of crystal growth normal to that plane).

Trace elements, therefore, may have a significant effect upon crystal morphology; and crystal morphology, conversely, may provide an indication of the nature and amounts of trace elements present. A particularly good example of such a relationship is to be seen in the morphological contrast between normal and cesium-bearing beryl. The former occurs characteristically as simple hexagonal prisms with planar (pinacoidal) terminations, and the latter frequently exhibits a tabular configuration with complex (pyramidal) terminations.

Other physical properties of minerals, including refractive indices, specific gravity, birefringence, atomic spacing and unit cell dimensions, have been found to vary systematically within isomorphous mineral series (e.g., the plagioclase feldspars and the olivines) whose compositions may vary through solid solution involving two or more of the essential elemental constituents. It is likely, there-

fore, that variations in trace element content would produce comparable effects, though probably on a much smaller scale.

Unfortunately, the possible effects of trace element concentrations upon the physical properties of common rock-forming minerals have not been systematically investigated to any great extent. Moreover, it is known that other factors may effect both the internal structure and external morphology of mineral crystals (e.g., the temperature-dependent  $\alpha - \beta$  transformation in quartz and the pressure-dependent quartz-coesite transformation), and it is entirely possible that these might mask any influences exerted by trace elements.

#### GEOLOGIC AGE AND TRACE ELEMENT DISTRIBUTION

Many variations in elemental distribution are known to have occurred during the course of geologic time.<sup>14</sup> In most mining districts, for example, ore deposition has taken place during a very limited span of time and is, therefore, restricted to formations or structures of a particular geologic age. Similarly, detailed studies within specific "petrogenetic provinces" have indicated that trace element distributions and concentrations may vary systematically from oldest to youngest rocks.<sup>15-18</sup> This variation reflects the progress and the relative effectiveness through time of the various igneous, sedimentary, and metamorphic processes of geochemical differentiation which have accompanied regional petrogenesis. Such local observations have given rise to suggestions concerning the possibility of systematic variations in elemental concentration and distribution on a worldwide scale and throughout the entire course of

geologic time. These speculations, however, involve such gross geological and cosmological generalizations and assumptions that they are of no value in predicting elemental concentrations in rocks of any specific region or age.

On the other hand, even a rudimentary knowledge of regional geological history may be of some significance in defining magmatic affiliations, sources of sediments, rates of weathering and erosion, etc., all of which are of at least potential significance as determinants of trace element concentrations.

## SUMMARY

This chapter briefly outlines a number of geological factors which are known or

thought to influence trace element distributions in rock. Of all these factors the one whose effects are most evident and definable is host rock mineralogy.

Because trace element distribution is related to rock mineralogy, and because the mineralogical analysis of a rock is usually far simpler, faster and less expensive than an exhaustive chemical analysis, consistent mineralogical associations of trace elements, if they can be defined, offer a convenient means of estimating trace element concentrations in rock. Conversely, if mineralogical affinities of trace elements are not considered, there may be little or no rational basis for predicting trace element concentrations in rocks for which specific analytical data are not available.

# Concentrations Of Selected Trace Elements In Common Rock Types

## A SUMMARY OF PUBLISHED ANALYTICAL DATA

The ranges of reported concentrations for each of twenty-nine trace elements in seven representative varieties of rock are tabulated in Table I. In order to obtain as large a data population as possible, secondary compilations and tabulations as well as primary sources were used in preparing this table. Where possible, however, the maximum and minimum values reported for each rock type have been traced to their primary sources for verification of their analytical reliability and geological validity.

In accordance with the standards accepted in most recent compilations of trace

element data, analyses made prior to 1940 have been excluded from consideration except in a few cases where only a limited number of analyses were available, and where the advantages to be gained through an increase in data population were likely to outweigh the disadvantages of analytical imprecision.

In order to minimize the possibility of errors resulting from nonrepresentative sampling, analyses of extremely uncommon rock types have been generally eliminated from consideration. Analyses of specimens taken from the immediate vicinity of ore deposits, where substantial chemical addition, subtraction, and redistribution may be assumed to have taken

| Element            | Rock Type <sup>a</sup>                      |   |   |   |   |   |  |   |  |   | Maximum<br>Ore Deposit<br>Concentration <sup>c</sup> | Maximum Mineralogical Concentration <sup>c</sup> |   |   |  |  |
|--------------------|---|---|---|---|---|---|--|---|--|---|--|--|---|---|--|--|
|                    | Fenag<br>Number of<br>Analyses <sup>c</sup> | Range of<br>Concentrations <sup>c</sup> | Cold-Frag<br>Number of<br>Analyses <sup>c</sup> | Range of<br>Concentrations <sup>c</sup> | Self-Calcic<br>Number of<br>Analyses <sup>c</sup> | Range of<br>Concentrations <sup>c</sup>   | Sil-Potassic<br>Number of<br>Analyses <sup>c</sup> | Range of<br>Concentrations <sup>c</sup> | Alumino-Potassic<br>Number of<br>Analyses <sup>c</sup> | Range of<br>Concentrations <sup>c</sup> |  |  | Siliceous<br>Number of<br>Analyses <sup>c</sup> | Range of<br>Concentrations <sup>c</sup> | Calcareous<br>Number of<br>Analyses <sup>c</sup>   | Range of<br>Concentrations <sup>c</sup>  |
| Antimony           | 3 <sup>+</sup>                              | 0.1 - 0.2                               | 35 <sup>+</sup>                                 | 0.039 - 1.4                             | 5 <sup>+</sup>                                    | 0.1 - 3                                   | 33 <sup>+</sup>                                    | 0.1 - 5                                 | ?  | 0.0 <sup>d</sup>                        | ?  | 0.1 - 0.6 <sup>e</sup>                           | 0.3 - 1.2 <sup>e</sup>                          | 41%                                     | Native Sb (100%)   |  |
| Arsenic            | 33 <sup>+</sup>                             | 0.3 - 15.8                              | 141 <sup>+</sup>                                | 0.3 - 32                                | 42 <sup>+</sup>                                   | 0.5 - 12.5                                | 123 <sup>+</sup>                                   | 0.5 - 14                                | ?  | 1.4 <sup>e</sup>                        | ?  | 0.67 <sup>e</sup> - 3 <sup>e</sup>               | 0.67 - 3  | 23%                                     | Native As (100%)   |  |
| Barium             | 248 <sup>+</sup>                            | 0.4 - 5000                              | 399 <sup>+</sup>                                | 10 - 2000                               | 50 <sup>+</sup>                                   | 150 - 3000                                | 147 <sup>+</sup>                                   | 12.5 - 3000                             | 147 <sup>+</sup>                                       | 100 - 1600                              | 658 <sup>+</sup>                                     | 938 <sup>e</sup> - 1500 <sup>e</sup>             | 127 <sup>e</sup> - 207 <sup>e</sup>             | 41%                                     | Barite - BaSO <sub>4</sub> - (9%)  |  |
| Beryllium          | 35 <sup>+</sup>                             | <0.2 - 5 <sup>e</sup>                   | 151 <sup>+</sup>                                | <0.2 - 5 <sup>e</sup>                   | 52 <sup>+</sup>                                   | 1.6 <sup>e</sup> - 14                     | 580 <sup>+</sup>                                   | 1.8 - 500                               | 168 <sup>+</sup>                                       | 1 - 50                                  | 85 <sup>+</sup>                                      | 1.8 - 5 <sup>e</sup>                             | 0.7 - 3   | 1.25%                                   | Phenakite - Be <sub>2</sub> SiO <sub>4</sub> - (14.4%)   |  |
| Bismuth            | 1   | 1.2                                     | 27 <sup>+</sup>                                 | 0.007 - 2                               | 1   | 1   | 15 <sup>+</sup>                                    | 0.01 - 2                                | 4 <sup>+</sup>   | 0.0 - 0.09                              | 4 <sup>+</sup>                                       | 0.09 <sup>e</sup> - 0.25 <sup>e</sup>            | 0.09 <sup>e</sup> - 0.25 <sup>e</sup>           | 25%                                     | Native Bi (100%)   |  |
| Cerium             | 4 <sup>+</sup>                              | 1.4 - 750                               | 140 <sup>+</sup>                                | 1.08 - 131.3                            | 6 <sup>+</sup>                                    | 22.5 - 170                                | 22 <sup>+</sup>                                    | 1.67 - 2300                             | 17 <sup>+</sup>  | 0.7 - 2400                              | 18 <sup>+</sup>                                      | 1.34 - 144                                       | 1.05 - 63                                       | 15 - 70                                 |  |  |
| Cesium             | 4 <sup>+</sup>                              | 0.0013 - 160                            | 55 <sup>+</sup>                                 | 0.17 - 10                               | 13 <sup>+</sup>                                   | 0.17 - 10                                 | 107 <sup>+</sup>                                   | 1 - 115                                 | 41 <sup>+</sup>  | 0.8 - 25                                | 18 <sup>+</sup>                                      | 1.34 - 144                                       | 1.05 - 63                                       | 21%                                     | Pollucite - Cs <sub>4</sub> Al <sub>3</sub> Si <sub>3</sub> O <sub>12</sub> · H <sub>2</sub> O - (45%) |  |
| Cobalt             | 18 <sup>+</sup>                             | 0.021 - 24                              | 81 <sup>+</sup>                                 | 0.015 - 0.5                             | 2 <sup>+</sup>                                    | 0.0038 <sup>e</sup> - 0.0046 <sup>e</sup> | 17 <sup>+</sup>                                    | 0.0029 - 1.1                            | ?  | 0.0004 <sup>e</sup>                     | ?  | 0.00038 <sup>e</sup> - 0.00038 <sup>e</sup>      | 0.00038 <sup>e</sup> - 0.00038 <sup>e</sup>     | 0.7%                                    | Native Co (100%)   |  |
| Copper             | 18 <sup>+</sup>                             | 0.01 - 8                                | 15 <sup>+</sup>                                 | <0.05 - 0.98                            | 7 <sup>+</sup>                                    | 0.017 - 1.9                               | 75 <sup>+</sup>                                    | <0.05 - 0.98                            | ?  | 0.00008 - 0.00008                       | ?  | 0.00008 - 0.00008                                | 0.00008 - 0.00008                               | 0.7%                                    | Native Cu (100%)   |  |
| Fluorine           | 4 <sup>+</sup>                              | 0.01 - 8                                | 15 <sup>+</sup>                                 | <0.05 - 0.98                            | 7 <sup>+</sup>                                    | 0.01 - 0.98                               | 75 <sup>+</sup>                                    | <0.05 - 0.98                            | ?  | 0.00008 - 0.00008                       | ?  | 0.00008 - 0.00008                                | 0.00008 - 0.00008                               | 0.7%                                    | Native F (100%)  |  |
| Iodine             | 4 <sup>+</sup>                              | 0.01 - 8                                | 15 <sup>+</sup>                                 | <0.05 - 0.98                            | 7 <sup>+</sup>                                    | 0.01 - 0.98                               | 75 <sup>+</sup>                                    | <0.05 - 0.98                            | ?  | 0.00008 - 0.00008                       | ?  | 0.00008 - 0.00008                                | 0.00008 - 0.00008                               | 0.7%                                    | Native I (100%)  |  |
| Lead               | 12 <sup>+</sup>                             | 0.01 - 42                               | 238 <sup>+</sup>                                | 0.035 - 53                              | 116 <sup>+</sup>                                  | 2 - 70                                    | 265 <sup>+</sup>                                   | 0.01 - 400                              | 68 <sup>+</sup>  | 3 - 118                                 | 491 <sup>+</sup>                                     | 1 - 120  | 184 <sup>+</sup>                                | 6.4%                                    | Monazite - (Ce, La, Y, Th) PO <sub>4</sub> - (up to 10.0%)   |  |
| Molybdenum         | 35 <sup>+</sup>                             | 0.05 - 10                               | 153 <sup>+</sup>                                | 0.075 - 7.3                             | 208 <sup>+</sup>                                  | <0.2 - 5.6                                | 548 <sup>+</sup>                                   | 0.1 - 280                               | 15 <sup>+</sup>  | 0.5 - 5.5                               | 252 <sup>+</sup>                                     | <0.2 - 1000                                      | 49 <sup>+</sup>                                 | 25%                                     | Native Mo (100%)   |  |
| Nickel (Columbium) | 18 <sup>+</sup>                             | 0.02 - 1050                             | 32 <sup>+</sup>                                 | 0.007 - 170                             | 38 <sup>+</sup>                                   | 0.25 - 110                                | 223 <sup>+</sup>                                   | 0.14 - 700                              | 65 <sup>+</sup>  | 10 - 1600                               | 42 <sup>+</sup>                                      | 0.00008 - 2.5                                    | 4 <sup>+</sup>                                  | 5.9%                                    | Nickeliferous - Ni <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> - (9%)                                  |  |
| Palladium          | 500 <sup>+</sup>                            | 0.002 - 12                              | 13 <sup>+</sup>                                 | 0.018 <sup>e</sup> - 1.9                | ?   | 0.002 <sup>e</sup> - 1.9                  | 6 <sup>+</sup>                                     | 0.0018 <sup>e</sup> - 0.01              | ?  | 0.00043                                 | ?  | 0.00008 - 2.5                                    | 4 <sup>+</sup>                                  | 2.9%                                    | Nickeliferous - Ni <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> - (9%)                                  |  |
| Platinum           | 500 <sup>+</sup>                            | 0.002 - 12                              | 13 <sup>+</sup>                                 | 0.018 <sup>e</sup> - 1.9                | ?   | 0.002 <sup>e</sup> - 1.9                  | 6 <sup>+</sup>                                     | 0.0018 <sup>e</sup> - 0.01              | ?  | 0.00043                                 | ?  | 0.00008 - 2.5                                    | 4 <sup>+</sup>                                  | 0.01%                                   | Native Pt - (100%)   |  |
| Praseodymium       | 3 <sup>+</sup>                              | 0.22 - 77                               | 131 <sup>+</sup>                                | 0.37 - 13                               | 4 <sup>+</sup>                                    | 0.37 - 13                                 | 16 <sup>+</sup>                                    | 0.0082 - 0.02                           | ?  | 0.00032                                 | 200 <sup>+</sup>                                     | 0.0082 - 0.03                                    | 0.0082 - 0.03                                   | 0.003%                                  | Native Pr - (100%)   |  |
| Rhenium            | 500 <sup>+</sup>                            | 0.0004 - 1                              | 1 <sup>+</sup>                                  | 0.00029 - 0.06                          | ?   | 0.00029 - 0.06                            | ?  | 0.00029 - 0.06                          | ?  | 0.00018                                 | ?  | 0.00029 - 0.03                                   | 0.00029 - 0.03                                  | 2.7%                                    | Monazite - (Ce, La, Y, Th) PO <sub>4</sub> - (up to 4.5% as diadochic proxy)                           |  |
| Rhodium            | 500 <sup>+</sup>                            | 0.0004 - 1                              | 1 <sup>+</sup>                                  | 0.00029 - 0.06                          | ?   | 0.00029 - 0.06                            | ?  | 0.00029 - 0.06                          | ?  | 0.00018                                 | ?  | 0.00029 - 0.03                                   | 0.00029 - 0.03                                  | 2.7%                                    | Monazite - (Ce, La, Y, Th) PO <sub>4</sub> - (up to 4.5% as diadochic proxy)                           |  |
| Rubidium           | 26 <sup>+</sup>                             | 0.2 - 12                                | 445 <sup>+</sup>                                | ?                                       | ?   | ?   | ?  | ?                                       | ?  | ?                                       | ?  | ?  | ?   | ?                                       | 0.00005%   | Iron-bearing - (Fe, Al, Si, Ti) PO <sub>4</sub> - (up to 12% as diadochic proxy) |
| Sr                 | 17 <sup>+</sup>                             | 0.002 - 0.3                             | ?   | <0.4                                    | ?   | <0.4                                      | ?  | <0.4                                    | ?  | <0.4                                    | ?  | <0.4   | ?   | ?                                       | 2%   | Iron-bearing - (Fe, Al, Si, Ti) PO <sub>4</sub> - (up to 12% as diadochic proxy) |
| Strontium          | 284 <sup>+</sup>                            | 1 - 5000                                | 279 <sup>+</sup>                                | 4.2 - 4500                              | 55 <sup>+</sup>                                   | 47 - 4000                                 | 465 <sup>+</sup>                                   | 8 - 1300                                | 153 <sup>+</sup>                                       | 5 - 4200                                | 817 <sup>+</sup>                                     | 10 - 1500  | 777 <sup>+</sup>                                | 41%                                     | Iron-bearing - (Fe, Al, Si, Ti) PO <sub>4</sub> - (up to 12% as diadochic proxy)                       |  |
| Tantalum           | 3 <sup>+</sup>                              | 0.49 - 1                                | 16 <sup>+</sup>                                 | 0.48 <sup>e</sup> - 1.1                 | ?   | 0.1 - 3.5                                 | 97 <sup>+</sup>                                    | 0.8 <sup>e</sup> - 32                   | 49 <sup>+</sup>  | 2.1 - 135                               | 23 <sup>+</sup>                                      | 0.2 - 3.6  | ?   | ?                                       | 0.00005%   | Iron-bearing - (Fe, Al, Si, Ti) PO <sub>4</sub> - (up to 12% as diadochic proxy) |
| Tellurium          | ?   | 0.001                                   | 2 <sup>+</sup>                                  | 0.001 - 0.02                            | ?   | 0.001                                     | 2 <sup>+</sup>                                     | 0.001 - 0.02                            | ?  | 0.001                                   | ?  | 0.001  | ?   | ?                                       | 0.00005%   | Iron-bearing - (Fe, Al, Si, Ti) PO <sub>4</sub> - (up to 12% as diadochic proxy) |
| Tin                | 8 <sup>+</sup>                              | 0.3 - 1.3                               | 89 <sup>+</sup>                                 | 0.3 - 100                               | 77 <sup>+</sup>                                   | 1.5 - 45                                  | 285 <sup>+</sup>                                   | 1 - 440                                 | 29 <sup>+</sup>  | 1.8 - 30                                | 32 <sup>+</sup>                                      | 1.5 - 260  | 3 <sup>+</sup>                                  | ?                                       | 0.00005%   | Iron-bearing - (Fe, Al, Si, Ti) PO <sub>4</sub> - (up to 12% as diadochic proxy) |
| Tungsten           | 21 <sup>+</sup>                             | 0.33 - 6.3                              | 49 <sup>+</sup>                                 | <0.2 - 24                               | 13 <sup>+</sup>                                   | 1.3 - 270                                 | 199 <sup>+</sup>                                   | 1.3 - 270                               | 24 <sup>+</sup>  | 0.7 - 25.9                              | 2000 <sup>+</sup>                                    | <0.2 - 128                                       | 2000 <sup>+</sup>                               | 8%                                      | Native Sn - (100%)   |  |
| Uranium            | 17 <sup>+</sup>                             | 0.001 - 0.2                             | 795 <sup>+</sup>                                | 0.02 - 20                               | 364 <sup>+</sup>                                  | 0.1 - 70                                  | 803 <sup>+</sup>                                   | 0.07 - 470                              | 250 <sup>+</sup>                                       | 0.1 - 89                                | 468 <sup>+</sup>                                     | 0.1 - 5000                                       | 109 <sup>+</sup>                                | 15%                                     | Tungstenite - WSi <sub>2</sub> - (74%)   |  |
| Vanadium           | 8 <sup>+</sup>                              | 0.3 - 20                                | 568 <sup>+</sup>                                | 2.3 - 390                               | 183 <sup>+</sup>                                  | 16 - 300                                  | 311 <sup>+</sup>                                   | 7.3 - 1000                              | 40 <sup>+</sup>  | 7.9 - 1100                              | 239 <sup>+</sup>                                     | 8 - 380  | 12 <sup>+</sup>                                 | 0.45%                                   | Uraninite - UO <sub>2</sub> - (89%)  |  |
| Yttrium            | 20 <sup>+</sup>                             | 2 - 400                                 | 585 <sup>+</sup>                                | 2 - 1500                                | 96 <sup>+</sup>                                   | 20 - 3000                                 | 233 <sup>+</sup>                                   | 12 - 3000                               | 9 <sup>+</sup>   | 120 - 1500                              | 258 <sup>+</sup>                                     | 9 - 3100   | 128 <sup>+</sup>                                | 0.59%                                   | Xenotime - YPO <sub>4</sub> - (41%)  |  |
| Zirconium          | 20 <sup>+</sup>                             | 2 - 400                                 | 585 <sup>+</sup>                                | 2 - 1500                                | 96 <sup>+</sup>                                   | 20 - 3000                                 | 233 <sup>+</sup>                                   | 12 - 3000                               | 9 <sup>+</sup>   | 120 - 1500                              | 258 <sup>+</sup>                                     | 9 - 3100   | 128 <sup>+</sup>                                | 0.59%                                   | Bastnaesite - Y <sub>2</sub> SiO <sub>7</sub> - (85%)  |  |

<sup>a</sup>See Tables II and III

<sup>b</sup>See pp. 8-13.

<sup>c</sup>Parts per million

<sup>d</sup>Order-of-magnitude estimate

<sup>e</sup>Average value, range not reported

Table I. Concentrations of selected trace elements in rocks. (See App. C for the sources of analytical data.)

place, have likewise been eliminated.

Where accurate data are available, extreme (ore deposit) enrichments of trace elements are noted in Table I as approximations of the absolute maximum concentrations to be anticipated in a sizeable mass of rock under even the most extraordinary circumstances. Still higher concentrations, however, may be encountered in specimens of individual minerals. These mineralogical maxima are also noted in Table I.

Absolute minimum concentrations of any trace element, under the influence of appropriate processes of geochemical segregation (e.g., fractional crystallization, differential solution, selective weathering, transportation and deposition of sediments, hydrothermal metasomatism, etc.) may be assumed to approximate zero.

Table I also indicates the range of concentrations reported for each element in recent analyses of the standard rocks G-1 and W-1 (see p. 9 ). This range may be regarded as the best available indication of the reliability of analytical data for a given element.

Because trace element concentrations are closely related to host rock mineralogy, which is only indirectly related to the mode of rock origin (sedimentary, metamorphic, or igneous), a system of rock classification based upon mineralogical or chemical composition is probably more appropriate for the defining of trace element distribution trends than is the more traditional petrogenetic classification. For example, the grouping of sandstone, quartzite, and silexite (sedimentary, metamorphic, and igneous rocks, respectively, composed largely or entirely of  $\text{SiO}_2$  in the mineralogical form of quartz)

into a "siliceous" category would probably contribute more to a consistent and meaningful geochemical interpretation than would their separation into three different petrogenetic groups. Accordingly, Table I groups various common rock types into seven compositional categories. The chemical and mineralogical characteristics of these categories, and the common rock types included in each category, are indicated in Table II. Table III gives the chemical formulas of minerals listed in Table II.

#### RELIABILITY OF PUBLISHED ANALYTICAL DATA

As Ahrens<sup>19</sup> has pointed out, "the real value of . . . the data of geochemistry depends both on its quantity and its quality. Although we will always wish for yet more information, the amount that has accumulated is vast: our immediate concern is the quality of this information."

Although painstaking attention has been paid to the details of analytical procedures in the laboratory, a comparison of even the most recent and best analyses performed on identical standard rock samples prepared by the U. S. Geological Survey (G-1, granite; and W-1, diabase) shows that experimental errors may be of disturbing magnitude, particularly within the concentration range of the trace elements.<sup>20-24</sup> Ahrens<sup>19</sup> has demonstrated an inverse correlation between the concentration of various elements and the accuracy of analytical data pertaining to those elements. His data suggest that the relative deviation of analytical values for elemental concentrations of about 1 ppm may encompass several orders of magnitude. It seems probable, however, that

Table II. Compositional categories employed in Table I.

| Compositional category | Primary chemical characteristic                            | Typical minerals <sup>a</sup>                   | Typical rocks   |
|------------------------|--|---|---|
| Femag                  | Rich in Fe and Mg  | Amphibole, pyroxene, olivine                    | Dunite, peridotite, pyroxenite, amphibolite, "ultramafic" rocks, "ultrabasic" rocks       |
| Calci-Femag            | Rich in Ca, Fe, and Mg                                     | Calcic plagioclase, pyroxene                    | Gabbro, diabase, basalt, norite, anorthosite, dark gneisses, "mafic" rocks, "basic" rocks |
| Sodi-Calcic            | Containing approximately equal amounts of Ca and Na        | Intermediate plagioclase, amphibole, orthoclase | Diorite, granodiorite, dacite, latite, andesite, "intermediate" rocks                     |
| Sial-Potassic          | Rich in Si, Al, K  | Orthoclase, sodic plagioclase, amphibole        | Granite, rhyolite, syenite, nepheline syenite, phonolite, "acidic" rocks                  |
| Aluminous              | Rich in Al   | Montmorillonite, illite, muscovite              | Clay, shale, slate, phyllite, schist  |
| Siliceous              | Composed largely of SiO <sub>2</sub>                       | Quartz, chalcedony                              | Sandstone, quartzite, chert   |
| Calcareous             | Composed largely of CaCO <sub>3</sub> or MgCO <sub>3</sub> | Calcite, aragonite, dolomite                    | Limestone, marble, dolomite   |

<sup>a</sup>See Table III for chemical formulas of these minerals.

despite (or because of) this inherent inaccuracy the available data can at least provide reliable approximations of the maximum and minimum trace element concentrations in various major rock types. The significance of any modal or normative values drawn from these data, however, must remain a matter of conjecture.

#### VALIDITY OF PUBLISHED ANALYTICAL DATA

It is a well-established fact, particularly in the field of mining geology where accurate analytical data are of immediate monetary significance, that the determination of rock composition involves far more than the consideration of a few "grab samples," because the

composition and other properties of a given rock may vary significantly from point to point even within the limited confines of a single stope. Moreover, even the most skillful and painstaking analyses are of no value if the samples submitted for assay are deliberately "salted" or prejudicially selected. The geochemical literature, however, is replete with analytical determinations based upon samples selected precisely because of their unusual petrology, or because of their association with ore deposits or other peculiar elemental concentrations within the earth's crust. Still other analyses, reputedly representing the composition of a batholith, a sedimentary stratum, or other extensive rock unit, are sometimes presented without validating or

Table III. Chemical formulas of minerals listed in Table II.

|                 |   |
|-----------------|---|
| Amphibole       | $\text{Ca}_2\text{Na}(\text{Mg}, \text{Fe})_4(\text{Al}, \text{Fe}, \text{Ti})_3\text{Si}_6\text{O}_{22}(\text{O}, \text{OH})_2$                            |
| Aragonite       | $\text{CaCO}_3$   |
| Calcite         | $\text{CaCO}_3$   |
| Chalcedony      | $\text{SiO}_2$  |
| Dolomite        | $\text{CaMg}(\text{CO}_3)_2$  |
| Illite          | $(\text{OH})_4\text{K}_x(\text{Al}_4\cdot\text{Fe}_4\cdot\text{Mg}_4\cdot\text{Mg}_6)\text{Si}_{8-x}\cdot\text{Al}_x\text{O}_{20} \text{ (x = 1.0 to 1.5)}$ |
| Montmorillonite | $(\text{OH})_4\text{Al}_4\text{Si}_8\text{O}_{10}\cdot x\text{H}_2\text{O}$   |
| Muscovite       | $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$   |
| Olivine         | $(\text{Mg}, \text{Fe})_2\text{SiO}_4$  |
| Orthoclase      | $\text{KAlSi}_3\text{O}_8$  |
| Plagioclase     | $(\text{Na}, \text{Ca})\text{Al}(\text{Si}, \text{Al})\text{Si}_2\text{O}_8$  |
| Pyroxene        | $\text{Ca}(\text{Mg}, \text{Fe}, \text{Al})(\text{Al}, \text{Si})_2\text{O}_6$  |
| Quartz          | $\text{SiO}_2$  |

even identifying the precise nature and origin of the samples used.

In general, therefore, one cannot make any a priori assumption as to whether the validity of the available data extends beyond the individual specimens selected for analysis. Such an extension may be presumed only if (1) the mineralogy of the analytical specimen is known, (2) the mineralogical affinity of trace elements can be established, and (3) a mineralogical similarity can be drawn between the analytical sample and its suspected analog. Even when these conditions have been met, there is still a possibility that trace element concentrations might vary between mineralogically identical specimens formed at different times, in different places, and with qualitatively and quantitatively different "stockpiles" of trace elements to draw upon.

## Predictive Trace Element Data

### PREDICTIVE USE OF GEOCHEMICAL DATA

A qualitative approach to the problem of predicting trace element concentrations in rocks has been illustrated on pages 3-5. The analytical data presented in Table I and the detailed descriptive data included in App. A provide a basis for more precise and more quantitative trace element predictions.

As an example, one might consider a prediction of rubidium concentrations in an unweathered diorite having the following gross mineralogical composition:

|                          |     |
|--------------------------|-----|
| Intermediate Plagioclase | 50% |
| Amphibole                | 35% |
| Pyroxene                 | 10% |
| Quartz                   | 5%  |

With reference to Table II, it can be seen that this rock would fall within the sodi-calcic composition category. The reported range of rubidium concentrations for rocks of this category (see Table I) is 1-1,000 ppm. Because the mineralogical composition of the rock more closely resembles that of the calci-femag group than that of the sial-potassic group (see Table II), and because calci-femag rocks are likely

to contain less rubidium than sodi-calcic rocks (see Table I), it is likely that the rubidium content of the diorite falls in the lower portion of the reported sodi-calcic range (i.e., between 1 and 500 ppm). Moreover, because rubidium occurs in rocks chiefly as a diadochic replacement of potassium (see page 24), and because there are no potash-bearing minerals reported in the diorite, it may be inferred that the rubidium content of this rock probably falls in the lower portion of this more restricted range (i.e., between 1 and 250 ppm).

A more extensive example of a trace element prediction, involving an actual rock specimen and evaluated with reference to analytical data for the same specimen, is presented in the next section.

#### A TRACE ELEMENT PREDICTION WITH ANALYTICAL CORROBORATION

In order to test the validity of data and concepts presented in this report, it was suggested that trace element predictions be made for a specific rock so that the accuracy of these predictions might be evaluated by comparison with the results of subsequent chemical analyses. The medium selected for consideration was a plutonic rock of the Mesozoic Sierra Nevada Batholith from the U. S. Army Corps of Engineers Buchanan Dam site, about 35 miles north of Fresno, California.

A preliminary trace element prediction was based upon data obtained from megascopic examination of a single hand specimen (core section) taken from a depth of 357.1 ft in a drill hole located at 272,670.1 N; 2,150,476 E.\*

\*California Lambert coordinate system, zone 3.

Megascopic examination indicates that this rock is a light-gray medium-grained (average grain size: 1 - 2 mm) equigranular granitoid rock (probably granite or quartz monzonite) with the following estimated mineralogical composition:

|           |     |
|-----------|-----|
| Feldspar  | 60% |
| Quartz    | 25% |
| Biotite   | 10% |
| Muscovite | 1%  |
| Sericite  | 1%  |
| Chlorite  | 1%  |

Localized limonitic stains and smears of metallic material on the surface of the core are assumed to have been caused by contact between the rock and the core barrel or other ferrous hardware.

On the basis of this megascopic examination, the rock appears to fall within the sial-potassic compositional category as defined in Table II, but would probably lie close to the sodi-calcic end of the sial-potassic compositional range.

With these considerations in mind, a prediction of trace element concentrations was made, utilizing the analytical data presented in Table I and the predictive procedure outlined in the previous section. This prediction is presented in Table IV.

Subsequent to the megascopic examination of the single core specimen from the Buchanan Dam site and the preparation of a trace element prediction based upon this examination, the writer reviewed several published reports dealing with the geology and petrology of the Sierra Nevada batholith in the general vicinity of the Buchanan Dam site. At that time a petrographic thin section was also prepared from the original core specimen, and was examined microscopically by the writer. Logs of several



test borings in the vicinity of the dam site were also reviewed.

Logs describing approximately 2285 linear ft of core from borings in the immediate vicinity of the Buchanan Dam site

Table IV. Estimates of trace element concentrations for Buchanan Dam site, based upon megascopic examination of hand specimen and the predictive procedures outlined on page 14.

| Element             | Concentration (ppm)                     |
|---------------------|---|
| Antimony            | 0.1 - 3.0                               |
| Arsenic             | 0.5 - 5.0                               |
| Barium              | 12.5 - 1000                             |
| Beryllium           | 1.8 - 10                                |
| Bismuth             | 0.01 - 1                                |
| Cerium              | 1.67 - 500                              |
| Cesium              | 1.0 - 20                                |
| Gold                | 0.0004 - 0.10                           |
| Indium              | 0.02 - 1.0                              |
| Iodine              | 0.05 - 0.5                              |
| Lanthanum           | 1.0 - 300                               |
| Lead                | 0.01 - 200                              |
| Molybdenum          | 0.1 - 100                               |
| Niobium (Columbium) | 0.1 - 30                                |
| Palladium           | 0.0016 - 0.01                           |
| Platinum            | 0.0082 - 0.01                           |
| Praesodymium        | 0.19 - 30                               |
| Rhenium             | 0.00022 - 0.001                         |
| Rhodium             | 0.00X <sup>a</sup> - 0.1                |
| Rubidium            | 1.0 - 1000                              |
| Ruthenium           | 0.000X <sup>a</sup> - 0.0X <sup>a</sup> |
| Strontium           | 50 - 1000                               |
| Tantalum            | 0.9 - 10                                |
| Tellurium           | 0.001 - 0.1                             |
| Tin                 | 1.0 - 50                                |
| Tungsten            | 1.3 - 50                                |
| Uranium             | 0.07 - 50                               |
| Yttrium             | 7.8 - 100                               |
| Zirconium           | 12 - 1500                               |

<sup>a</sup>Order-of-magnitude estimate.

indicate that the plutonic rock is quite uniform throughout the area. A few variations in composition (pegmatitic veinlets, biotitic segregations, and localized narrow zones of argillic or sericitic alteration) are noted at irregular intervals; but the number and size of such variations is such as to be of no significance with respect to the overall composition of the plutonic mass.

Decomposition due to weathering is noted in surficial exposures at the dam site, but seldom extends to depths greater than 10 ft in the core borings. Some effects of weathering, however, are noted along open joints or fractures to depths in excess of 100 ft. The most noticeable effects of weathering are the development of limonitic staining (attributed to the partial or complete decomposition of biotite) and pitting (probably due to the decomposition of plagioclase).

Some joints or fractures are found to have been filled by calcareous material which may be of hydrothermal or supergene origin.

There are no published references which describe the specific plutonic rocks of the Buchanan Dam site. Very similar rocks have, however, been described in nearby areas. These similar plutonic rocks have been variously described as biotite quartz monzonite,<sup>25</sup> biotite granodiorite,<sup>26</sup> and granite.<sup>27</sup> It should be noted, however, that the "granite of arch rock" described in Ref. 27 contains plagioclase feldspar in excess of potash feldspar and should, accordingly, be designated as a quartz monzonite or granodiorite rather than a granite.

On the basis of a microscopic examination of the prepared petrographic thin

section, the mineralogical composition of the specimen appears to be:

|  |     |
|--|-----|
| Feldspar                                       | 70% |
| Quartz   | 20% |
| Biotite  | 5%  |
| Chlorite                                       | 1%  |
| Sericite                                       | 1%  |
| Apatite  | 1%  |
| Argillic alteration products (kaolinite, etc.) | 1%  |

These observations are in general agreement with the tentative conclusions drawn earlier on the basis of megascopic examination. Microscopic examination, however, indicates that a substantial portion of the feldspar present (>50%) is plagioclase. Many of the plagioclase grains show concentric zoning and/or development of combined albite and pericline twinning. Because of the plagioclase:K-spar ratio, this rock cannot be properly classified as a granite. It is a quartz monzonite or granodiorite.

The incipient to moderate degree of argillic and sericitic alteration of feldspars, and the local alteration of biotite to chlorite, are regarded as indications of epigenetic metasomatism.

References 26, 28, 29 note that economically significant deposits of tungsten, copper, and silica (massive quartz veins) are found within 15 miles of the Buchanan Dam site. Tungsten mineralization, as described in Ref. 26, is most typically located near the margins of quartz monzonite or granodiorite plutons, and is associated with subeconomic concentrations

of copper, arsenic, and molybdenum sulfide minerals.

The additional data obtained from boring logs, published reports, and thin section examination generally confirm the assumptions made in preparing the estimates of trace element concentrations presented in Table IV. Published references to metallic mineral concentrations which are genetically related to plutonic rocks of the Sierra Nevada batholith and spatially related to the Buchanan Dam site, however, suggest that the concentrations of certain metallic elements (Sb, As, Bi, In, Pb, Mo, Re, Sn, W) might tend to fall in the upper portions of the predicted range.

After the predictions of trace element concentrations (Table IV) had been prepared, spectrochemical analyses were performed by the Lawrence Radiation Laboratory to determine the concentrations of ten of the trace elements considered in this report. The results of these analyses are shown in Table V. In six cases where numerical values for trace element concentrations were obtained (Ba, Be, La, Pb, Sr, and Zr), these values

Table V. Trace element concentrations (ppm) for Buchanan Dam site specimen, as determined by Lawrence Radiation Laboratory spectrochemical analysis.<sup>a</sup>

|           |      |            |     |
|-----------|------|------------|-----|
| Barium    | 1000 | Molybdenum | <10 |
| Beryllium | 2    | Strontium  | 400 |
| Cerium    | <40  | Tin        | <3  |
| Lanthanum | 15   | Yttrium    | <10 |
| Lead      | 10   | Zirconium  | 150 |

<sup>a</sup>These emission-spectrographic analyses are considered to be accurate to  $\pm 50\%$  for concentrations over 10 ppm and  $\pm 100\%$  for concentrations less than 10 ppm.

were found to fall within the predicted range indicated in Table IV. In the other four cases, (Ce, Mo, Sn, and Y), the trace element concentrations were below the threshold sensitivity of the analytical procedures employed, but it seems probable that the actual concentrations of these elements would fall within the predicted ranges because:

1. In each case the threshold sensitivity of the analytical method lies well below the upper limit of the predicted range.

2. In each case the lower limit of the predicted range represents the minimum concentration reported in published analyses for rocks of the same compositional category (see Table I).

## Conclusions

On the basis of the data presented in this report, it is concluded that:

1. Trace element concentration varies from rock type to rock type in a defineable and systematic fashion.

2. The factors controlling trace element distribution in rocks can, for the most part, be understood in terms of basic and well-established geochemical principles.

3. The primary factor governing the distribution of trace elements in rock is the mineralogy of the host rock.

These conclusions, in turn, suggest that:

1. A qualitative estimate of the trace element content of a rock can be made by relating that rock to the compositional categories described in Table II and to the various petrogenetic environments and processes considered in App. A.

2. A semiquantitative estimate of the trace element content of a rock can be made by correlating:

- a. The range of absolute trace element concentrations reported for rocks of the same compositional category (Table I), and

- b. The mineralogy of the particular rock, and its favorable or adverse influence

with respect to the concentration of specific trace elements.

3. A quantitative estimate of the range of possible trace element concentrations in a rock may be made with reference to the maximum and minimum concentrations reported in analytical data (Table I) for rocks of the same compositional category.

4. Standard "whole rock" chemical analyses, although they yield precise and accurate compositional data for the particular specimens analysed, may provide no reliable basis for estimating elemental concentrations in other rock types or other portions of the same rock formation.

The general validity of the predictive method outlined in this report is evidenced by the agreement (as reported in the previous section) between predicted concentrations and analytical results for the same test specimen. Further substantiation of methodological validity should be sought through additional comparisons of predictive and analytical data for a variety of rock types. Eventually, if this predictive approach proves to be consistently valid, an effort should be made to refine the method so as to improve the degree of predictive precision.

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## Appendix A

### GEOCHEMICAL BEHAVIOR OF SELECTED TRACE ELEMENTS

| <u>Element</u>                | <u>Page No.</u> |
|-------------------------------|-----------------|
| Antimony . . . . .            | A-2             |
| Arsenic . . . . .             | A-2             |
| Barium . . . . .              | A-3             |
| Beryllium . . . . .           | A-4             |
| Bismuth . . . . .             | A-2             |
| Cerium . . . . .              | A-7             |
| Cesium . . . . .              | A-5             |
| Gold . . . . .                | A-8             |
| Indium . . . . .              | A-9             |
| Iodine . . . . .              | A-10            |
| Lanthanum . . . . .           | A-7             |
| Lead . . . . .                | A-11            |
| Molybdenum . . . . .          | A-12            |
| Niobium (Columbium) . . . . . | A-13            |
| Palladium . . . . .           | A-14            |
| Platinum . . . . .            | A-14            |
| Praesodymium . . . . .        | A-7             |
| Rhenium . . . . .             | A-15            |
| Rhodium . . . . .             | A-14            |
| Rubidium . . . . .            | A-5             |
| Ruthenium . . . . .           | A-14            |
| Strontium . . . . .           | A-3             |
| Tantalum . . . . .            | A-13            |
| Tellurium . . . . .           | A-15            |
| Tin . . . . .                 | A-16            |
| Tungsten . . . . .            | A-17            |
| Uranium . . . . .             | A-18            |
| Yttrium . . . . .             | A-7             |
| Zirconium . . . . .           | A-19            |

This appendix summarizes the salient geochemical characteristics of each of the twenty-nine trace elements considered in this study. Insofar as the available data permit, the following aspects of geochemical behavior are outlined for each element:

1. Behavior under magmatic conditions.
2. Behavior under conditions of weathering and sedimentation.
3. Behavior under metamorphic conditions.
4. Behavior in the biosphere.

The information included in this Appendix is a summary of relevant data found in all or most standard reference tests of geochemistry. Specific references have been cited only in the case of information which is not common to most standard reference texts.

### ARSENIC, ANTIMONY, AND BISMUTH

These three elements, listed above in order of decreasing abundance, are strongly chalcophile. Aside from the rare bismuth silicate mineral, eulytite— $\text{Bi}_4(\text{SiO}_4)_3$ —none of these elements is known to occur as a stoichiometric constituent of any silicate mineral structure. Arsenic is known to substitute for phosphorus in apatite, but the amount of such diadochy and the extent, if any, of parallel behavior on the part of antimony or bismuth, is not well documented.

Although all three of these elements are chalcophile (associated particularly with sulfides of copper, iron, nickel, and cobalt), only arsenic is consistently concentrated in those high temperature sulfide deposits which have formed as a result of early magmatic fractionation. These elements are more typically concentrated in low temperature hydrothermal (epithermal) sulfide deposits, where they may occur as stoichiometric constituents of sulfide and sulfo-salt minerals or as diadochic inclusions in common base metal sulfides.

The behavior of these elements under conditions of weathering and sedimentation is not well documented. Arsenic is commonly associated with iron and manganese in sedimentary deposits (probably due to adsorption by metallic hydroxides), and it is thought that antimony and bismuth may behave similarly.<sup>2, 30</sup> All three elements tend to be concentrated in argillaceous sediments as compared with other rock types—a fact which may reflect their association with iron or manganese hydroxides, their adsorption by colloidal materials or clay minerals, and their affinity for sulfide minerals which might form in the same sedimentary environment.

Rankama and Sahama<sup>2</sup> state that arsenic is removed from sedimentary rocks during metamorphism, but no specific evidence is cited to support this contention. The occurrence of arsenical minerals in and near metamorphosed sulfide deposits at Ammerberg, Sweden, and at Kongsberg, Skutterud, and Snarnum, Norway, suggest that the total arsenic content of large rock masses (and the concentrations of other

chalcophile elements, including antimony and bismuth), is not markedly altered during regional metamorphism, though remobilization and recrystallization may produce localized concentrations within a larger geochemical system.

Some evidence of arsenic, antimony, and bismuth concentrations above the average crustal abundance have been reported in various plant and animal tissues,<sup>2</sup> but the precise nature, degree, biological role, or possible geological significance of such concentrations is not documented in the geochemical literature. Patty<sup>31</sup> reports that the greatest arsenic concentrations in human victims of arsenic poisoning are found in the hair, and notes that antimony is most likely to be concentrated in the thyroid (up to 88 ppm) and adrenal glands.

## BARIUM AND STRONTIUM

These elements exhibit a generally lithophile behavior. Although the similarity of certain chemical characteristics, including electrovalence, would suggest a close geochemical association of strontium and barium with calcium, such a relationship is largely precluded by the marked disparities in ionic radii, particularly between calcium and barium. The ionic radii of both strontium and barium, however, are similar to that of potassium. Accordingly, the geochemical behavior of these elements (especially barium) is governed largely by the potash content of potential host minerals. Electrostatic equilibrium is probably maintained, during substitution of divalent strontium or barium ions for univalent potassium ions, by a decrease in the Si:O ratio.

Because of its additional though limited ability to proxy for calcium, strontium is a more ubiquitous trace element than barium, and may occur in appreciable concentrations in apatite, pyroxene, and amphibole as well as in the various members of the feldspar group. The feldspars, which are the most abundant minerals in most igneous rocks and which include both calcium and potassium-bearing members, are the most important loci of barium and strontium concentration in igneous rocks. Rarely, under conditions of extreme magmatic fractionation or unusually alkalic magma composition, strontium or barium may become sufficiently concentrated to occur as stoichiometric constituents of distinctive mineral species.

Under weathering conditions, both strontium and barium are likely to be dissolved and carried away in aqueous bicarbonate, chloride, or sulfate solutions, and are, therefore, present only very sparingly in residual sediments. Barium, which is readily adsorbed by clay minerals, is likely to be removed from solution rather promptly, and concentrated in argillaceous sediments. Strontium, being less amenable to clay adsorption, is likely to remain in solution until removed by evaporation, chemical precipitation, or biochemical activity.

The geochemical significance of strontium/calcium diadochy in limestones is far less than might be expected, because the solubility of strontium in the calcite

crystal structure is extremely limited. The strontium content of limestones is generally proportional to the amount of biogenetic material included in the rock, because the crystal lattice of biogenetic  $\text{CaCO}_3$  (aragonite) is a less closely packed structure than that of calcite and can, therefore, more readily accommodate the incorporation of larger strontium ions. Moreover, because the aragonite crystal structure is metastable and eventually inverts to the more stable calcite structure, the total amount of aragonite (and diadochic strontium) in a limestone is likely to diminish with time. The strontium liberated during the aragonite-calcite transformation may be removed in solution, or fixed as a stoichiometric constituent in discrete grains of celestite or strontianite. Thus, the total strontium content of a limestone is likely to diminish and the ratio of stoichiometric:diadochic strontium is likely to increase with the age of the host rock.

A comparison of strontium concentrations in dolomitic and non-dolomitic limestones suggests that the dolomite crystal structure is even less tolerant than that of calcite to the presence of this proxy element. Thus, dolomitization, which generally increases with time in limestones, is another mechanism which may be at least partially responsible for the inverse correlation between strontium content and age of sedimentary carbonate rocks.

Extensive stratified deposits of barite and celestite are known in many parts of the world, and are a primary economic source of barium and strontium, respectively. Such deposits probably represent concentrations of these elements which were originally present in biogenetic limestones, but were exsolved from calcareous skeletal materials during the aragonite-calcite inversion and fixed in the diagenetic sedimentary environment by sulfate-rich solutions.

To the extent that it involves only a recrystallization of pre-existing rock material, metamorphism would have little influence upon strontium or barium concentrations. In the thermal environment of metamorphism, however, and in the presence of sulfate or carbonate solutions, it is quite possible that these trace elements might be removed from rock-forming silicate minerals and reconstituted to form crystals of barite, celestite, strontianite, etc. Under conditions of metasomatism, on the other hand, barium and strontium might be significantly redistributed as a result of their susceptibility to aqueous solution and transport.

Patty<sup>31</sup> has reported strontium concentrations of up to 11.8 ppm in normal mammalian (rat) bone tissue, and barium concentrations of up to 24 ppm in human ash.

## BERYLLIUM

The geochemical behavior of beryllium in igneous rocks is markedly lithophile, and is governed largely by the possibility and limitations of  $\text{Be}^{+2}/\text{Si}^{+4}$  diadochy in rock-forming minerals. Such substitution of beryllium for silicon in silicate crystal



lattices, though quite feasible from the standpoint of similar ionic radii, is limited by the electrostatic disequilibrium introduced with the substitution of a divalent for a tetravalent cation. This restriction may be somewhat offset in compositionally complex mafic silicates by coupled diadochy involving high valence cations (especially  $Zr^{+4}$ ,  $Ti^{+4}$ ,  $Nb^{+4}$ ,  $Ta^{+4}$ ) or univalent anions (especially  $F^-$ ,  $OH^-$ ).<sup>32</sup>

Because of the restrictions on Be/Si diadochy, beryllium becomes progressively concentrated in residual liquids as magmatic fractionation proceeds, and is, therefore, most abundant in the granites, syenites, aplites, and pegmatites formed from such residual magmas. Beryllium occurs most typically in these rocks as a stoichiometric constituent of beryl or other beryllium silicate minerals.

The mafic silicate minerals which are most likely to contain diadochic beryllium are relatively unstable under weathering conditions. Diadochic beryllium is, therefore, taken into solution in the weathering environment and transported to areas of sedimentary accumulation where it is likely to be fixed by clay mineral adsorption in shales and argillaceous limestones. Stoichiometric beryllium silicates, in contrast, are notably resistant to chemical weathering, and are likely to be concentrated in residual or alluvial deposits.

To the extent that the chemical and physical properties of solutions in a metamorphic or metasomatic environment might approximate those of residual magmatic solutions, appreciable solution and redistribution of beryllium might be expected. To the extent that such a process is operative, a slight increase in the stoichiometric:diadochic beryllium ratio might be anticipated. These assumptions are substantiated by the existence of large metasomatic replacement bodies of stoichiometric beryllium minerals.

Neither the organic role of beryllium nor the possibility of biogenetic concentrations have been extensively investigated by geochemists. Several forms of organic (plant) ash, however, have been reported to contain beryllium concentrations of up to 2%.<sup>2</sup> Patty<sup>31</sup> has reported beryllium concentrations of up to several hundred ppm in the lung tissue of beryllium poisoning victims. It should be noted, however, that the beryllium compounds responsible for industrial poisoning are soluble, and therefore are far more readily assimilated by organisms than any naturally occurring beryllium-bearing mineral.

## CESIUM AND RUBIDIUM

Cesium and rubidium, like the other more abundant alkali metals (sodium and potassium), display an unusually strong affinity of oxygen. Thus, they tend to become fixed in oxy-salt minerals, such as silicates, and are classified, accordingly, as lithophile elements. Like other lithophile elements, the alkali metals are concentrated most abundantly in the oxygen-rich sialic rocks of the earth's crust (e.g., granites, rhyolites, syenites, and their sedimentary and metamorphic derivatives).

The strongly ionic bonding characteristics of the alkali metals, which may largely account for their concentration in late-stage, relatively low-temperature magmatic differentiates, also exert a controlling influence upon the behavior of these elements under conditions of weathering, sedimentation, and metamorphism. The ready solubility of alkali metal ions in aqueous solutions results in a marked impoverishment of these elements in most weathering residua, although rubidium concentrations of up to 4,000 ppm have been reported in residual soils overlying a pegmatite.<sup>33</sup> Adsorption of these elements by several of the common clay minerals leads to a high alkali content in many argillaceous sediments, and correspondingly low concentration of these elements in sea water and in evaporite deposits.

To the extent that metamorphism or metasomatism involves the action of aqueous solutions, the readily soluble alkali metals are likely to undergo significant remobilization and redistribution.

Though rubidium and cesium are not generally regarded as biophile elements, (and are, in fact, noted for their toxicity), marked concentrations of these elements occur in certain organic materials. Significant quantities of rubidium are found in certain plants including oak, beet, tea, tobacco, and several varieties of seaweed.<sup>34</sup> Concentrations of up to 2000 ppm rubidium in soil<sup>2</sup> and up to 250 ppm cesium in fossil trilobites<sup>35</sup> are particularly noteworthy in that they are nearly twice as great as those reported in rocks of any type (see Table I). Fairhall<sup>36</sup> notes that rubidium concentrations in humans are most likely to occur in cardiac and skeletal tissue, and that cesium is most likely to be concentrated in the retina.

The only common element for which rubidium or cesium can proxy to any appreciable extent in mineral structures is potassium. Thus, it is the common potash-bearing, rock-forming minerals (e.g., orthoclase, microcline, muscovite, and biotite) which are most likely to be enriched in the rare alkalis. Rubidium, because of its greater similarity to potassium (particularly with regard to ionic radius), is more readily incorporated into the lattice structures of potassic rock-forming minerals, and never reaches sufficient concentrations to become a stoichiometric constituent of any known mineral. The larger cesium ion is less readily incorporated into the structure of rock-forming potassic minerals. Accordingly, the cesium content of residual magmatic liquid increases progressively during the process of igneous differentiation until, under conditions of extreme magmatic fractionation, cesium may be sufficiently concentrated to form a distinctive mineral, pollucite. There is evidence that, because of the size discrepancy between cesium and potassium ions, the distribution of cesium may be less closely related to that of potassium than is the case with rubidium. Stavrov and Portnov<sup>37</sup> have suggested that cesium may concentrate in minerals having large open lattice structures, without regard to their potassium content. This suggestion is substantiated by the occurrence of cesium in concentrations of up to 3% in beryl<sup>38</sup> and by the concentration of cesium and the marked increase of the Cs:Rb ratio in biotite as compared to coexisting potash feldspar noted by Stavrov and Znamenskii<sup>39</sup> and by Slepnev.<sup>32</sup>

## CERIUM, YTTRIUM, LANTHANUM, AND PRAESODYMIUM

The "rare earth metals," including the four elements listed above in probable order of decreasing abundance, are not particularly rare in comparison to many other trace elements considered in this report. Their average concentrations in most common rocks are, in fact, substantially higher than those of many other elements of industrial, technical, and economic importance.

As might be inferred from their strongly lithophile character and from the similarity of the ionic radii between the trivalent rare earths and divalent calcium, there is a potential for rare earth/calcium diadochy in the crystal structures of several common rock-forming minerals, (provided that coupled substitutions or omissions can maintain the electrostatic equilibrium of the crystal lattice). Consistently high rare earth concentrations in apatite indicate that its crystal structure provides the most favorable sites for such diadochic substitution; but substantial concentrations of rare earth elements (yttrium in particular) have also been reported in plagioclase, hornblende, "ugrandite" garnets, and other common calcium-bearing minerals.

Biotite and potash feldspar have also been found to contain significant concentrations of the rare earths, probably as diadochic replacements of potassium; and, despite the dissimilarities of respective ionic radii,\* the possibility of rare earth diadochy with iron and magnesium has been suggested.<sup>40</sup>

Substantial substitution of trivalent rare earths for tetravalent elements such as uranium, thorium, zirconium, tantalum, and niobium have been reported, but the concentration of these elements in rocks is generally so small that this possible diadochy is of little or no compositional significance.

The discrepancies between the chemical and physical properties of calcium and those of the rare earth elements is sufficient to limit the extent of possible diadochy and to produce an increasing degree of rare earth concentration in residual magmatic liquids. For this reason the maximum rare earth concentrations are found not in the calcium-rich rocks of the calci-femag or sodi-calcic groups, but in such late magmatic differentiates as granites, syenites, and their pegmatitic equivalents. In these sial-potassic and aluminopotassic rocks the rare earth elements occur primarily as stoichiometric constituents of such minerals as monazite, orthite, and allanite, though some rare earth/potassium diadochy may be evident in the feldspars and micas of these rocks as well.

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\*Effective ionic radii in complex silicate mineral structures may differ significantly from the simple ionic radii listed in published tabulations, and qualitative or quantitative predictions of diadochy based upon similarities of ionic radii must, therefore, be substantiated by empirical and experimental data before they can be considered reliable.

Diadochic rare earth elements may be set free from their mineralogical matrices under weathering conditions. Some of the rare earths thus released may be incorporated or adsorbed by clay minerals in an environment of argillic sedimentation. The rest are taken into ionic solution in ground and surface waters and carried to the sea, where rare earth/calcium diadochy may produce minor concentrations of the rare earths in limestones.

On the other hand, rare earth elements occurring as stoichiometric constituents of monazite (the most common rare earth mineral) behave quite differently during weathering and sedimentation. Monazite, being extremely resistant to both chemical and physical weathering, and having a specific gravity higher than that of most common rock-forming minerals, is typically associated with magnetite, ilmenite, rutile, zircon, and garnets in placer deposits. Rare earth concentrations of up to 27% have been reported in such deposits.<sup>8</sup>

No published data were found concerning the behavior of the rare earth elements under metamorphic conditions. To the extent, however, that solutions in the metamorphic environment approximate the physical and chemical characteristics of a late magmatic residual solution (a reasonable assumption, based upon both empirical and theoretical data) it seems likely that a slight increase in the stoichiometric:diadochic rare earth ratio would be achieved as a result of mineralogical re-equilibration under metamorphic conditions.

Although the presence of the rare earth elements in plant and animal tissues has been established,<sup>2</sup> no biological concentrations have been reported in the geochemical literature which would suggest preferential concentration of these elements by organisms.

## GOLD

Gold is a markedly chalcophile element. It occurs very sparsely, if at all, as a diadochic proxy in common rock forming minerals. It is typically associated with deposits of iron and copper sulfides formed during early or late magmatic fractionation. Gold concentrations of up to 100 ppm have been found in such sulfide minerals.

Despite its consistent association with metallic sulfides, no gold sulfide minerals are known. Gold occurs most commonly in nature as native metal (usually alloyed with at least 10% silver) which may be distributed in rock as masses of up to 100 lb or more, or, more commonly, as barely visible or microscopic disseminated grains. In a few deposits where tellurium is also concentrated, gold may be present together with various other cations as a stoichiometric constituent of metallic telluride minerals.

Although there is some evidence that gold may be sparingly soluble (probably as chloride or organic complexes) in surficial and ground waters, the characteristic chemical inertia of this element and the unusually high specific gravity of native gold

result in its concentration in sedimentary placer deposits along with magnetite, ilmenite, pyrite, and other heavy mineral particles. Concentrations of gold have also been reported in sulfide mineral deposits associated with euxinic shales, but the genesis of this gold is uncertain. It may represent finely divided detrital material, a chemical precipitate, or an epigenetic hydrothermal addition.

The chemical behavior of gold under metamorphic conditions is essentially unknown. To the extent that its chalcophile behavior remains constant under these conditions, however, it can probably be assumed that no more than minor and local redistribution of gold would occur.

Although the biological role of gold is not mentioned in the geochemical literature, this element has been found as a trace constituent in both plant and animal tissues. Gold concentrations of up to 60 ppm have been found in *Equisetum* plants (e.g. *E. arvense* and *F. palustre*) growing in the vicinity of auriferous ore deposits,<sup>2</sup> and it is probable that these represent biological enrichments in over ambient environmental concentrations. Gold concentrations of up to 0.03 ppm in marine animals, especially starfish,<sup>41</sup> definitely represent a biogenetic enrichment over environmental (sea water) concentrations.

## INDIUM

Indium is a strongly and consistently chalcophile element which is typically concentrated in sulfide minerals formed during early or later phases of magmatic fractionation. A limited degree of diadochy involving  $\text{In}^{+3}$  and  $\text{Fe}^{+2}$  is noted in rock-forming silicate minerals, especially the pyroxenes,<sup>2</sup> but the indium concentrations produced by such substitution are far less than those noted in sulfide mineral deposits.

Most occurrences of indium in sulfide minerals, as in rock-forming silicates, apparently involve  $\text{In}^{+3}/\text{Fe}^{+2}$  diadochy. Maximum indium concentrations of up to 10,000 ppm<sup>42</sup> are found in sphalerite ( $\text{ZnS}$ ) formed at high temperatures. Under these genetic conditions, substantial amounts of iron may replace zinc in the sphalerite lattice, and indium, in turn, may replace the iron. This substitution of trivalent indium for divalent iron necessitates electrostatic re-equilibration of the crystal structure. This requirement may account for the reported correlation of indium and silver contents in sulfide ores.<sup>43</sup> The occurrence of indium in iron-free sulfide minerals, including galena and tetrahedrite is less readily accounted for, although Badalov<sup>43</sup> notes that indium compounds have been prepared experimentally which are isostructural with most of these minerals. A fairly persistent geochemical association of indium with tin is also reported, especially in the oxide mineral cassiterite.<sup>42,44,45</sup>

Because most indium-bearing minerals are readily decomposed under conditions of chemical weathering, the indium content of weathered rock is likely to be gradually dissipated in aqueous solutions. However, the chalcophile character of indium and

the propensity for In/Fe diadochy are likely to result in a reconcentration of this trace element in any authigenic sulfide minerals which might form in euxinic sediments or in sedimentary iron formations.

As is the case with the sulfide minerals in which it is most typically concentrated, indium is probably not affected by metamorphism except for minor local remobilization.

No information was found in the geochemical literature regarding possible biogenetic concentrations of indium, though the occurrence of indium in sedimentary sulfide or iron deposits may be at least indirectly governed by the biological processes of sulfur-fixing or iron-fixing microorganisms.

## IODINE

Though iodine is usually classified as a lithophile element along with the other halogens,<sup>2</sup> empirical considerations suggest that iodine may be more accurately regarded as being atmophile and biophile in character.

The radius of the iodine ion (large as compared even to the relatively large ionic radii of the other halogen elements) generally precludes substitution of iodine for other elements in igneous rock-forming mineral structures. The sparse iodine concentration in magmas prevents the nucleation and growth of any stoichiometric iodine minerals. Iodine is, accordingly, concentrated in late magmatic differentiates; but even there it is seldom if ever incorporated into any of the crystallizing mineral phases. It seems probable, therefore, that the minute quantities of iodine reported in aqueous and gaseous volcanic emanations represent essentially the entire iodine content of the parent magma.

Under weathering conditions, iodine may be extracted from the atmosphere or from ground or surface waters to form a number of rare iodide and iodate minerals [e.g. iodyrite—AgI; coccinite—HgI; lauterite— $\text{Ca}(\text{IO}_3)_2$ ; salesite— $\text{Cu}(\text{IO}_3)(\text{OH})$ ; dietzeite— $\text{Ca}_2(\text{IO}_3)_2\text{CrO}_4$ ]. The extreme solubility of these minerals in aqueous solutions, however, precludes their formation or persistence except in an extremely arid environment. The solubility of iodine and its inability to proxy in crystal structures for any more common element also precludes the mineralogical fixation of this element under metamorphic-metasomatic conditions, in an environment of sub-aqueous sedimentation, or even under conditions of terrestrial sedimentation (except in extremely arid climates).

Living organisms provide by far the most effective mechanism and loci for iodine enrichment. Concentrations of up to 80,000 ppm have been reported<sup>2</sup> in the tissues of certain marine coelenterates. Notable concentrations have also been reported in thyroxin, an amino acid found in the thyroid gland of higher animals. It has been noted, moreover, that the iodine content of sedimentary rocks varies

according to the amount of organic material present;<sup>30</sup> and it is likely that the iodine-rich brines reported in many oil fields and elsewhere are derived from biogenetic concentrations in the enclosing sedimentary rocks.

## LEAD

The geochemical behavior of lead is markedly and consistently chalcophile. Although the ionic radius and electrovalence of lead are such as to permit limited diadochy with calcium in such minerals as pyroxene, hornblende, and apatite; although Pb/K diadochy may yield lead concentrations of up to 100 ppm in potassic rock-forming silicates such as biotite and orthoclase;<sup>46</sup> and although lead is known to occur as a stoichiometric constituent of the rare silicate mineral barysilite— $\text{Pb}_3(\text{Si}_2\text{O}_7)$ ; this element is most typically concentrated in the common sulfide mineral galena— $\text{PbS}$ . Galena, though occasionally found as minute disseminated grains within igneous rocks (especially those of intermediate to acidic composition), is most characteristically concentrated along with other chalcophile elements in sulfide mineral deposits associated with intermediate to acidic igneous rocks.

Under weathering conditions, galena is readily oxidized to form anglesite— $\text{PbSO}_4$ , or altered in the presence of carbonate-rich solutions to cerussite— $\text{PbCO}_3$ . Because both of these weathering products are highly resistant to further chemical decomposition, little lead is released into ground or surface water solution during weathering. Instead, the bulk of this element is likely to be retained in weathering residua, which may show a significant enrichment in lead relative to other more readily soluble elements.

Any lead taken into ground or surface water solution under weathering conditions is likely to be reprecipitated as galena in the sulfide-rich organic shales of euxinic basins. A minor amount of lead may also be fixed in sedimentary rocks as a diadochic substitute for calcium in aragonite; and some additional concentration may result from adsorption of lead ions by clay minerals.

Little precise information is available regarding the behavior of lead under metamorphic or metasomatic conditions. It seems probably, however, that lead, like other chalcophile elements, may undergo local remobilization and redistribution under high temperatures and pressures. This assumption is generally confirmed by the difficulties and inaccuracies encountered in attempts to apply lead-alpha geochronology to rocks which have undergone metamorphism.

The geochemical literature attributes no biological function to lead other than that of a toxic agent; yet concentrations of this element in marine organisms (especially foraminifera, coelenterates, echinoderms, crustaceans, and molluscs) apparently represent preferential biogenetic enrichments of up to 2,600 times the average concentrations in sea water.<sup>47</sup>

## MOLYBDENUM

The geochemical behavior of molybdenum is strongly and consistently chalcophile. Thus, although minor diadochic substitution of molybdenum for titanium, iron, aluminum, or silicon is reported in magnetite-ilmenite and various mafic silicate minerals,<sup>48</sup> this element is characteristically concentrated in sulfide mineral deposits, and especially in those formed under late magmatic, pegmatitic, or hydrothermal-pneumatolytic conditions, where it typically occurs in the mineral molybdenite— $\text{MoS}_2$ .

Because molybdenum has a greater affinity for sulfur than most other metals, molybdenite may sometimes crystallize from late magmatic residual liquids prior to the release of hydrothermal fluids, and may thus occur as disseminated flakes within the parent intrusive mass, as well as (or instead of) in satellitic hydrothermal veins.

The occurrence, within sulfide ore deposits, of up to 300 and 1000 ppm molybdenum in sphalerite and chalcopyrite, respectively,<sup>10</sup> suggests the possibility of significant diadochy (in a sulfur-rich environment) between molybdenum and copper, iron, or zinc.

Under weathering conditions, molybdenite and most other molybdenum-bearing minerals are quite susceptible to chemical decomposition. Some of the molybdenum thus released may be oxidized within the immediate weathering environment to form relatively resistant molybdate minerals. Most of the molybdenum freed by chemical weathering, however, is dispersed into ground and surface water solutions, from which it may eventually be deposited, along with other chalcophile elements, in sulfide mineral concentrations associated with highly organic euxinic shales.

Little is known about the geochemical behavior of molybdenum under metamorphic or metasomatic conditions. It seems probable, however, that molybdenite, like most other sulfide minerals, would be subject to local remobilization and redistribution in the temperature and pressure environment of metamorphism.

Although the biological significance of molybdenum has not been thoroughly investigated by geochemists, this element is known to play a significant role in the life processes of several organisms. Rankama and Sahama<sup>2</sup> note that molybdenum is essential for certain fungi and nitrogen-fixing microorganisms. Meulen<sup>49</sup> has reported molybdenum concentrations of up to 9 ppm in peas and beans, and Goldschmidt<sup>4</sup> has reported concentrations in the root nodules of various leguminosae. These facts provide further evidence that molybdenum may play a significant role in the process of nitrogen fixation.

Concentrations of up to 96 ppm molybdenum have also been reported in various types of plants growing in molybdenum-rich soils,<sup>50</sup> but it is not clear whether these represent selective biogenetic enrichments over the molybdenum content of the soils.

According to Meulen,<sup>49</sup> maximum molybdenum content of animal tissues is on the order of 1.5 ppm in the livers of pigs and oxen, though it cannot be determined on the basis of Meulen's data whether these concentrations represent a biogenetic enrichment



relative to the animals' geochemical environment or food intake. However, in reporting a molybdenum content of 0.12 ppm in cod liver, Meulen specifically notes that this represents a significant enrichment over ambient environmental concentrations. Krauskopf<sup>47</sup> has reported biogenetic concentrations of molybdenum in marine organisms which represent enrichments of up to 6,000 times the normal sea water concentrations of this element.

## NIOBIUM (COLUMBIUM) AND TANTALUM

These two elements bear a strong resemblance to one another in their chemical and physical behavior, and are typically associated with one another in their geological occurrences. Both niobium and tantalum show a strongly lithophile geochemical affinity.

When, as is usually the case, niobium and tantalum are present in magmatic melts in concentrations of 1 ppm or less, their distribution in the mineralogical products of magmatic crystallization is governed by limited diadochy with titanium and zirconium. It is noteworthy, however, that titaniferous magnetite-ilmenite ore deposits, which are generally regarded as early high-temperature magmatic segregations, are nearly devoid of niobium and tantalum, while the more sparsely distributed titanium minerals of later low-temperature magmatic differentiates are substantially enriched in these trace elements. The highest reported concentrations of niobium and tantalum are encountered in pegmatites which probably have crystallized from the final residual liquid resulting from extreme magmatic fractionation. Here these elements typically occur as stoichiometric constituents of complex multiple-oxide minerals such as columbite, tantalite, samarskite, and pyrochlore.

The inverse correlation which seems to exist between temperature of formation and the extent of niobium-tantalum diadochy in titanium and zirconium minerals is noteworthy in that it contradicts the generally valid principle that high-temperature crystal structures are more tolerant of diadochic inclusions than are low-temperature lattices. It has been suggested<sup>51</sup> that the governing factor in this particular case is the need for preserving electrostatic equilibrium within the crystal lattice while divalent niobium or tantalum is substituted for tetravalent titanium or zirconium. This electrostatic adjustment could, perhaps, be accomplished most readily through concomitant diadochy involving entry of univalent alkali metal ions into the affected crystal lattices; and the relatively high concentrations of alkalis in late-magmatic residual liquids would provide an optimum geochemical environment for such coupled substitution.

Though each of these two elements can and does substitute for several others (notably titanium) in various mineral structures, niobium is likely to be enriched (relative to tantalum) in the process of extreme magmatic fractionation. The governing factor here is probably the more highly covalent character of the Ta-O bond as compared to the Nb-O bond. This property enables tantalum to be included preferentially in

early-formed high-temperature mineral phases, with consequent increase in the Nb:Ta ratio of residual magma as fractionation proceeds. Thus, in the progressive fractionation of a magma having any given initial Ta:Nb ratio, one might expect to find this ratio higher in the earliest crystals formed, and lower in the residual liquid and those minerals eventually formed from it, than in the original melt.

Columbite and tantalite are the two most common minerals containing stoichiometric niobium and tantalum. Both are highly resistant to weathering and, like ilmenite, rutile, zircon, and other minerals in which appreciable concentrations of diadochic niobium or tantalum may be encountered, have specific gravities substantially higher than those of most rock-forming silicate minerals. Because of this, these two trace elements are likely to be enriched in clastic sedimentary rocks, and particularly in those which contain placer concentrations of high density minerals. However, Rankama and Sahama<sup>2</sup> note that argillic sediments and pelagic manganese nodules are sometimes found to be enriched in niobium and tantalum. This fact indicates that at least some migration and reconcentration of these elements may take place in an environment of weathering and sedimentation.

No data are available concerning the geochemical behavior of niobium and tantalum under metamorphic conditions. In view of their mineralogical affiliations, however, it seems unlikely that either the distribution or concentrations of these two elements would be significantly affected by metamorphism.

No preferential concentrations of niobium or tantalum have been reported as products of biological activities.

#### PLATINUM, PALLADIUM, RUTHENIUM, AND RHODIUM

The platinum metals, as a group, exhibit markedly siderophile behavior under magmatic conditions. They occur most frequently and most abundantly as native metals or metallic alloys in dunites, pyroxenites, and other ultramafic rocks. A definite though subordinate chalcophile tendency is also to be seen in the occurrence of these elements, with concentrations of the platinum metals (especially palladium) often occurring in early-magmatic massive sulfide deposits associated with mafic or ultramafic rocks. Igneous rocks of intermediate to acidic composition, and related hydrothermal vein deposits, are typically devoid of the platinum metals. High temperature hydrothermal-pneumatolytic vein deposits of cassiterite or molybdenite, however, may contain up to 1 ppm of the platinum metals.

Because of their high specific gravity and great resistance to chemical decomposition, the naturally occurring platinum metals and alloys are often enriched in residual or placer deposits derived from the weathering of ultramafic plutons. Minor concentrations of the platinum metals are also reported in some sedimentary manganese oxides and in some euxinic shales.

No data are available concerning the geochemical behavior of the platinum metals under metamorphic or metasomatic conditions. It does not seem likely, however, that any significant remobilization or redistribution of these elements would take place under the temperature and pressure conditions typical of dynamothermal metamorphism.

Little information is available in the geochemical literature regarding the biological role or possible biogenetic concentrations of the platinum metals. However, these elements have been found in the ashes of certain animals and plants.<sup>2</sup>

## RHENIUM

Although available data concerning the geochemistry of rhenium are limited and fragmentary, it appears that this element is consistently chalcophile in its behavior. Rhenium is most typically concentrated in sulfide mineral deposits. It is closely associated in almost all cases with molybdenite, which may contain up to 13,000 ppm rhenium.<sup>52</sup> However, other mineralogical associations of rhenium, including a concentration of 1000 ppm in uraninite, have also been noted.<sup>53</sup>

Studies of rhenium-bearing molybdenite deposits have led to the tentative conclusion that the rhenium content is greatest in those deposits thought to have been formed at highest temperatures and/or earliest in the crystallization history of sulfide-rich magmas,<sup>54</sup> and that rhenium concentrations may be correlated with both copper and tellurium contents of such deposits.<sup>53,55</sup> The persistent association of rhenium with molybdenite has led to the conclusion that  $\text{ReS}_2$ , which is not known to occur in nature, is isomorphous with  $\text{MoS}_2$ .

The occurrence of rhenium concentrations of up to 100 ppm in molybdenite from the Kupferschiefer ores of Mansfeld, Germany, suggests that rhenium may be released under weathering conditions, carried seaward in aqueous solution, and eventually precipitated along with other chalcophile elements in a low Eh, low pH environment. Because the syngenetic nature of the Kupferschiefer sulphides is a matter of some geological disagreement, however, this geochemical inference must be regarded as being somewhat speculative.

## TELLURIUM

Although data regarding the geochemical behavior of tellurium are extremely limited, one may conclude from the position of tellurium in the periodic table and its typical association with sulfide minerals that it is a strongly chalcophile element. As such, it is most likely to be concentrated, under magmatic conditions, in sulfide-rich differentiates which are characteristic of very early (ultramafic-mafic) or very late (pneumatolytic-hydrothermal) stages of magmatic differentiation. Tellurium, if present

in such sulfide concentrations, typically occurs as a stoichiometric constituent of metallic telluride minerals. Some diadochic substitution of tellurium for sulfur may also take place, as indicated by the occurrence of up to 595 ppm tellurium in iron-bearing sulfide minerals.<sup>56</sup>

Under weathering conditions, telluride minerals are normally oxidized to form tellurites or tellurates. Native tellurium, which is rare in nature, and which may oxidize to form the mineral tellurite— $\text{TeO}_2$ , may itself be a weathering product of primary metallic tellurides. The extent to which these oxidation products are chemically stable in the weathering environment is not accurately known. Markedly increased native gold contents in the oxidized portions of gold telluride ore deposits, however, suggest that a substantial percentage of the primary tellurium is removed in the course of the weathering process and carried seaward in aqueous solution. Upon reaching an environment of marine or terrestrial sedimentation, tellurium, if its chalcophile behavior is consistent, is likely to be concentrated in the sulfide-rich carbonaceous shales of euxinic basins.

No data are available concerning the effects of metamorphism upon the distribution of tellurium. To the extent that the geochemical behavior of this element parallels that of sulfur under such conditions, tellurium is likely to undergo significant local remobilization and concentration into metallic mineral segregations within shear zones, fold axes, or other structurally favorable sites.

#### TIN

Tin is reportedly capable of limited diadochy with Ti, Zr, Nb, Ta, Fe, and Ca under magmatic conditions.<sup>2</sup> Such substitutions, however, are of little significance with regard to average lithologic composition. The tin content of igneous rocks and their hydrothermal derivatives is governed primarily by the abundance of the mineral cassiterite— $\text{SnO}_2$ . Some diadochic tin is also found in a number of base-metal sulfide minerals. The tin content of magma generally increases during the process of fractionation and reaches a maximum in residual magmas and pneumatolytic-hydrothermal emanations. Concentrations of cassiterite in both igneous rocks and hydrothermal veins are typically accompanied by concentrations of fluorine (usually as tourmaline or topaz); which suggests that tin may be present in magmatic and hydrothermal solutions as a volatile fluoride complex.

Cassiterite has an unusually high density and a great resistance to both chemical decomposition and physical disintegration. Accordingly, this mineral is characteristically concentrated during weathering and sedimentation as unaltered grains in residual or placer sediments. Minor tin concentrations, probably resulting from clay mineral adsorption, are also reported in some argillic sediments.

No data are available concerning the behavior of tin under metamorphic or metasomatic conditions. The fact that primary tin concentrations are generally restricted to igneous rocks and high-temperature vein deposits, however, suggests that the distribution and concentration of this element would not be significantly altered under ordinary metamorphic conditions.

Although tin is reported to occur in both plant and animal tissues,<sup>2,57</sup> its precise biological role is not mentioned, nor is any indication given as to whether these occurrences represent preferential biogenetic enrichments over ambient environmental concentrations. Fairhall<sup>36</sup> reports that the presence of tin has been found to stimulate growth of fish.

## TUNGSTEN

Tungsten is similar to molybdenum in its chemical and physical properties, but differs significantly in its geochemical behavior and mineralogical associations. For example, under magmatic and hydrothermal conditions molybdenum is strongly chalcophile—occurring typically in the sulfide mineral molybdenite. Tungsten, however, occurs most frequently in tungstate minerals, especially scheelite— $\text{Ca}(\text{WO}_4)$ , although a tungsten sulfide mineral, tungstenite, is known to occur sparingly in nature.

Like molybdenum, tungsten rarely occurs as a diadochic substitution in common rock-forming silicate minerals. It is, therefore, progressively enriched during the process of magmatic fractionation and typically concentrated in the pneumatolytic-hydrothermal deposits produced by late stage magmatic emanations.

Although most tungstate minerals are fairly resistant to mechanical disintegration, they are readily dissolved in ground and surface waters. Precipitation from such solutions may give rise to minor secondary concentrations of tungsten, in the form of oxide or hydrous oxide minerals, within the zone of weathering. However, the bulk of the tungsten released during the weathering process remains in solution and is carried seaward.

The factors governing distribution and concentration of tungsten during sedimentation are generally unknown, and the available analytical data are inadequate to support any consistent hypothesis. It appears, however, that at least some tungsten may be precipitated in the presence of calcium-rich solutions; and tungsten concentrations of up to 7% have been reported<sup>2</sup> in sedimentary manganese oxides.

No data are available concerning the geochemical behavior of tungsten under metamorphic or metasomatic conditions. However, the ready solubility of tungstate minerals in aqueous solutions suggests the possibility of fairly extensive redistribution under such circumstances. Such redistribution would probably involve migration away from the temperature and pressure conditions of high-grade metamorphism and toward peripheral low-temperature "pressure shadow" zones.

Tungsten has been reported as a constituent of some marine animals,<sup>2</sup> but there is no indication in the geochemical literature as to the precise biological role of the element, or whether its occurrence in organisms represents a biogenetic enrichment in excess of ambient environmental concentrations. Tungsten concentrations have also been reported in plants growing over tungsten deposits.<sup>58</sup> Greatest concentrations, which are found in the root portions of such plants, apparently represent selective biogenetic concentrations over ambient (soil) concentrations. Patty<sup>31</sup> notes that tungsten concentrations in humans are most likely to be localized in bone, spleen, liver, or kidney tissue.

## URANIUM

The occurrence of uranium in igneous rocks is governed largely by  $U^{+4}/Ca^{+2}$  diadochy. The dissimilarity of these two elements with regard to electrovalence, however, severely limits the diadochic incorporation of uranium into the structures of most common rock-forming minerals, though appreciable concentrations have been reported in apatite, pyroxenes, and other compositionally complex minerals in which there is ample opportunity to make the necessary electrostatic adjustments through coupled substitution. Substitution of uranium for the rare earths, titanium, niobium, and tantalum may take place on a rather extensive scale; but such substitution is of little significance in terms of overall rock composition.

The consistent enrichment of uranium in granites and other acidic igneous rocks may be partly due to diadochic substitution of uranium for zirconium. Zhuraulev and Osipov<sup>59</sup>, however, note that plagioclase (in which uranium may substitute for calcium, with electrostatic equilibrium being maintained by coupled substitution of aluminum for silicon) holds more than 90 percent of the total uranium content in most acidic to intermediate igneous rocks.

Most of the uranium content of a magma is likely to remain in solution throughout the course of crystallization, thus becoming progressively enriched in the residual (pegmatitic and hydrothermal) magmatic liquids. Therefore, uranium is characteristically concentrated in pegmatites and in hydrothermal vein deposits, where it occurs most commonly as the oxide mineral uraninite (pitchblende). Uranium is typically associated in vein deposits with sulfides of copper, silver, or cobalt.

Uraninite is readily decomposed in an oxidizing environment. Thus, uranium is ordinarily taken into solution in ground and surface waters under weathering conditions. (The extensive uraninite deposits at Blind River, Ontario, and in the Witwatersrand District of South Africa are regarded by some geologists as representing placer accumulations in an oxygen-deficient environment; but it is equally possible that these deposits are the product of epigenetic hydrothermal mineralization.)

Intensive investigation of "Colorado Plateau Type" uranium deposits in sedimentary rocks has shown that uranium may be precipitated from ground or surface waters by a number of mechanisms including flow turbulence, pressure reduction, and ionic filtration through shale strata. The most strikingly effective agents in precipitating dissolved uranium, however, are  $H_2S$  and other reducing media generated by decaying organic matter. Thus, organic-rich black shales are typically enriched in uranium relative to other sedimentary rocks.

The uranium in sedimentary rocks is almost exclusively in the  $U^{+6}$  oxidation state, and occurs as a stoichiometric constituent of several dozen phosphates, vanadates, and other characteristic minerals.

There is little available information concerning the behavior of uranium under metamorphic or metasomatic conditions. It seems likely, however, that the relative solubility of uranium minerals would result in a migration of uranium-bearing solutions outward from centers of metamorphic activity—an assumption which is generally substantiated by observed radioactivity distribution patterns in regionally metamorphosed areas.<sup>60,61</sup>

Although the precise biological role of uranium is not described in the geochemical literature, biogenetic concentrations of the element have been reported in plant ash, fresh water algae, and in the thyroid glands of higher animals.<sup>2,57</sup> Malyuga<sup>57</sup> has noted that uranium adsorption is greatest in those plants whose root hair cell sap has a pH of 5.2 or less (as in the case of the conifers and various members of the rose family) and that the presence of uranium in plants is likely to increase the number of chromosomes in the cell nucleus. The occurrence of up to 300 ppm uranium in sedimentary apatite<sup>30</sup> and up to 4,500 ppm in fossil bones<sup>62</sup> suggests that U/Ca diadochy may give rise to significant concentrations of uranium in calcareous (and particularly in phosphatic) skeletal material. Such extraordinary concentrations are probably the result of epigenetic enrichment by uraniferous ground water rather than actual biogenetic concentrations. Elkins<sup>63</sup> has reported uranium concentrations of up to 17 ppm in normal bone tissue, and Patty<sup>31</sup> reports that the kidneys may also serve as loci of uranium concentration in higher animals.

## ZIRCONIUM

Zirconium is a strongly lithophile element, whose electrovalence and bonding characteristics are similar to those of silicon, and whose ionic radius is similar to those of iron and magnesium. The diadochic restrictions imposed by the combination of electrovalence, bonding characteristics, and ionic size, however, are such as to prevent significant substitution of zirconium for any of these elements in common rock-forming minerals. The possibility of extensive Zr/Nb-Ta diadochy is noted by Degenhardt<sup>64</sup> but such substitution is of little or no compositional significance in most common rock types.

Zirconium, therefore, tends to occur chiefly as a stoichiometric constituent of its own characteristic minerals (especially zircon) rather than as a diadochic proxy in more common rock-forming silicates. Because of this tendency, and because of the probable low ("average crust") concentration of zirconium in primary magmatic melts, the zirconium content of early mafic differentiates is quite low, while that of later sialic and alkalic differentiates is significantly higher.

Under weathering conditions zircon is singularly resistant to both physical disintegration and chemical decomposition. Thus zirconium, as zircon, is characteristically concentrated in sandstones along with quartz, garnet, magnetite, and other chemically and physically stable minerals.

To the extent that zirconium may be taken into solution during the weathering process, it is likely to be subsequently removed from solution through adsorption by clay minerals or ferric hydroxide—a fact which probably accounts for the presence of zirconium in argillic sediments and for the correlation between zirconium content and the amount of iron and argillic material in limestones.<sup>30</sup>

Although no specific data are available concerning the geochemical behavior of zirconium under metamorphic conditions, petrographic studies indicate that the zirconium (zircon) content of rocks is essentially unaffected by even the most intense metamorphism or metasomatism.

Zirconium is reported to occur both in organic soils and in living plant tissues<sup>1</sup> but no evidence is cited to indicate whether such occurrences represent preferential biogenetic enrichments in excess of ambient concentrations in the immediate geochemical environment.



## Appendix B

### GLOSSARY OF GEOLOGICAL AND GEOCHEMICAL TERMS

#### ACIDIC

Pertaining to volcanic or plutonic rocks rich in silica ( $\geq 66\%$   $\text{SiO}_2$ ), as contrasted with intermediate, basic (mafic), or ultrabasic (ultramafic) rocks. Generally synonymous with sialic.

#### ADSORPTION

Adhesion of molecules or ions to the surfaces of solid bodies with which they are in contact.

#### ALKALIC

Pertaining to volcanic or plutonic rocks whose alkali content is high relative to silica content (molecular ratio of  $> 1:6$ ). Such rocks are ordinarily characterized by the absence of free silica (quartz) and by the presence of feldspathoid minerals (e. g. nepheline, leucite).

#### ARGILLACEOUS

Pertaining to sedimentary and metasedimentary rocks rich in clay minerals (e. g. illite, montmorillonite) (see pelitic).

#### ARGILLIC

Synonym for argillaceous.

#### ATMOPHILE

Pertaining to those elements which are generally associated with the gaseous elements of the earth's atmosphere.

#### AUTHIGENIC

Pertaining to minerals or other substances formed in sedimentary material after deposition as a result of chemical or biochemical action, in contrast to materials (allogenic) transported from outside of the immediate depositional environment.

## BASIC

Pertaining to volcanic and plutonic rocks that have a comparatively low silica content (>55%), as contrasted with intermediate or acidic (sialic) rocks.

## BIOPHILE

Pertaining to elements generally concentrated in organisms.

## CHALCOPHILE

Pertaining to those elements which have a strong chemical affinity for sulfur, and which commonly occur in, or in association with, sulfide minerals.

## CLASTIC

Pertaining to those sedimentary rocks (e. g. shales, sandstones, and conglomerates) composed largely or entirely of fragmental materials, as distinct from chemical or biochemical precipitates.

## DIADOCHY

Replacement or replaceability of one atom or ion by another in a crystal lattice.

## DIAGENETIC

Pertaining to those processes which occur in sedimentary accumulations after deposition, but prior to consolidation.

## EARLY MAGMATIC

Pertaining to the initial high-temperature states of magmatic fractionation.

## Eh

A parameter of oxidation-reduction potential. (High Eh indicates an oxidizing environment; low Eh is characteristic of a reducing environment.)

## EPIGENETIC

Pertaining to mineral deposits of later origin than the enclosing rocks, in contrast to syngenetic deposits.

## EPITHERMAL

Pertaining to mineral deposits thought to have been formed by near-surface low-temperature hydrothermal activity.

#### EUXINIC

Pertaining to a low Eh, low pH sedimentary environment developed in isolated marine basins as a result of restricted circulation.

#### HYDROTHERMAL

Pertaining to hot aqueous solutions (generally thought to be of magmatic origin) and to the mineral deposits and rock alteration produced by such solutions.

#### INTERMEDIATE

Pertaining to volcanic or plutonic rocks having a silica content of  $>55$  and  $<66\%$  (see acidic, basic).

#### LITHOPHILE

Pertaining to elements generally occurring in, or associated with, the common rock-forming silicate minerals of the earth's crust.

#### LATE MAGMATIC

Pertaining to the final preconsolidational stages of magmatic fractionation.

#### MAFIC

Pertaining to volcanic or plutonic rocks composed largely of iron-rich and magnesium-rich silicate minerals. Generally synonymous with basic.

#### MAGMA

Naturally occurring hot mobile rock material, including variable proportions of a liquid silicate (melt or mutual solution) phase, suspended solid phases, and a gaseous phase.

#### MAGMATIC FRACTIONATION

Progressive changes in the composition of a magma due to removal of one or more of the coexisting phases (e. g. removal of a solid phase by sinking of high density crystals, removal of a gaseous phase by release of confining pressure). Essentially synonymous with magmatic differentiation.

## METAMORPHISM

A postformational process in which rock texture and/or mineralogy is altered by external agents, especially heat and pressure. Transformations as a result of weathering are not included in this concept. Metamorphism is generally regarded as a "closed system" process in which the total chemical composition of the affected rock is not changed (see metasomatism).

## METASOMATISM

A postformational process in which rock composition is altered by the addition and/or removal of chemical constituents (see metamorphism). Compositional changes resulting from weathering are not included in this concept.

## METASTABLE

Pertaining to the condition of a phase which exists temporarily outside of its equilibrium field during the process of spontaneous transformation to a phase which is in equilibrium under the existing conditions. A piece of ice floating in hot water is an example of a metastable phase.

## PEGMATITIC

Pertaining to a volatile-rich residual magma thought to represent a penultimate stage of magmatic fractionation. Also pertaining to abnormally coarse-grained acidic rock thought to be produced by consolidation of pegmatitic magma.

## PELAGIC

Pertaining to a deep water marine environment.

## PELITIC

Pertaining to sediments composed largely of clay-sized particles ( $>0.005\text{mm}$ ), and to sedimentary or metasedimentary rocks derived from such material. Often loosely used as a synonym for argillaceous.

## pH

A parameter of alkalinity or acidity, expressed as the negative logarithm of hydrogen ion activity. Low pH indicates acidic conditions; high pH indicates alkaline (basic) conditions. pH 7.0 indicates a condition of neutrality.

## PHASE

A homogeneous, physically distinguishable, or separable portion of matter within a nonhomogenous system.

## PLUTONIC

Pertaining to crystalline rocks formed at great depth, and having a granitoid texture, which are generally thought to be of magmatic origin.

## PNEUMATOLYTIC

Pertaining to late-stage volatile-rich magmatic emanations intermediate in character between pegmatitic and hydrothermal.

## SIALIC

Pertaining to volcanic or plutonic rocks rich in silica and alumina. Generally synonymous with acidic.

## SIDEROPHILE

Pertaining to elements which have a low affinity for oxygen and sulfur and are readily soluble in molten iron. Such elements are commonly concentrated in metallic meteorities, and are thought to be comparably concentrated in the earth's core.

## STOICHIOMETRIC

Pertaining to a definite chemical composition which can be expressed as a simple ratio of essential elemental constituents.

## SULFO-SALT

Minerals consisting of a metallic cation and an anionic complex consisting of an electropositive semi-metal, plus electronegative sulfur. (e.g., proustite— $\text{Ag}_3\text{AsS}_3$ ).

## SYNGENETIC

Pertaining to mineral deposits which are contemporaneous with the enclosing rocks, in contrast to epigenetic deposits.

## "UGRANDITE" GARNETS

An acronym referring to those members of the garnet group (uvarovite, grossularite, and andradite) containing calcium.

## ULTRAMAFIC

Pertaining to plutonic rocks composed entirely of metallic minerals and ferromagnesium silicates. Generally containing less than 48% silica. Synonymous with ultrabasic (see mafic, basic).

## Appendix C

### SOURCES OF ANALYTICAL DATA FOR TABLE I

Table I-C. Sources of analytical data for Table I.

| Element                | Reference numbers   |
|------------------------|---|
| Antimony               | 2, 4-6, 11, 18, 21, 22, 30, 33, 34, 65-80   |
| Arsenic                | 2, 4-6, 11, 21-23, 30, 33, 65, 66, 68, 69, 71, 72, 74-82  |
| Barium                 | 2, 4-6, 8, 15-18, 21, 22, 30, 33, 34, 42, 65-69, 71, 72, 74-80, 83-111  |
| Beryllium              | 2, 4-6, 18, 21, 22, 30, 32-34, 42, 46, 65, 66, 68, 69, 71, 72, 74-80, 87, 89, 90, 99, 101, 102, 108, 110, 112-118                           |
| Bismuth                | 2, 4-6, 11, 18, 21, 22, 33, 34, 47, 65, 66, 68, 69, 71-80, 90, 108, 119-123   |
| Cerium                 | 2, 4-6, 8, 18, 21, 22, 24, 30, 34, 40, 65, 66, 69, 71, 72, 74-81, 101, 108, 122-34  |
| Cesium                 | 2, 4, 6, 15, 21, 22, 30, 32, 34, 35, 37, 39, 65, 66, 68, 71, 72, 74-80, 83, 90, 94, 101, 135-146  |
| Gold                   | 2, 4-6, 10, 21-23, 30, 33, 42, 65, 66, 69, 71, 72, 74-80, 122, 147-149  |
| Indium                 | 2, 4, 6, 11, 21, 22, 30, 34, 43-45, 65, 66, 68, 71-77, 79, 80, 150-159  |
| Iodine                 | 2, 4-6, 21, 30, 65, 66, 69, 71, 72, 74, 76-80, 85, 160-168  |
| Lanthanum              | 2, 4, 8, 15, 16, 18, 21-24, 30, 33, 34, 40, 42, 65, 66, 69, 71, 72, 74, 76-81, 86, 87, 89, 94, 97, 99, 101, 106-108, 110, 111, 123-134, 169 |
| Lead                   | 2, 4-6, 10, 11, 15-18, 21, 22, 30, 33, 42, 46, 47, 65, 66, 68, 69, 71-80, 86, 87, 89, 90, 94, 96-99, 101, 102, 108, 109, 111, 139, 170-182  |
| Molybdenum             | 2, 4-6, 11, 15, 18, 21, 22, 30, 33, 34, 42, 46-49, 65, 66, 68, 69, 71, 72, 74-80, 87, 89, 90, 96-99, 106-108, 110, 111, 176, 183-193        |
| Niobium<br>(Columbium) | 2, 4, 5, 21, 33, 34, 51, 65-69, 71, 72, 74-80, 122, 142, 194-205  |
| Palladium              | 2, 4, 5, 21, 22, 34, 65, 66, 69, 71, 72, 76, 77, 79, 80, 206-208  |
| Platinum               | 2, 4-6, 11, 21, 65, 66, 69, 71, 72, 76-80, 149, 207-209   |
| Praesodymium           | 2, 4, 8, 21, 24, 30, 40, 65, 66, 71, 72, 74-80, 101, 123-131, 133, 134  |
| Rhenium                | 2, 4, 6, 11, 21, 22, 34, 52-55, 65, 66, 71, 72, 74, 76-80, 122, 210, 211  |
| Rhodium                | 2, 4-6, 21, 65, 66, 69, 71, 72, 76, 80, 207, 208  |

Table I-C. (Continued)

| Element   | Reference numbers  |
|-----------|--|
| Rubidium  | 2, 4, 6, 15-18, 21, 22, 30, 32, 34, 35, 39, 65-68, 71, 72, 74-80, 83, 86, 90, 92, 94, 96, 97, 99, 101, 106, 107, 109, 111, 122, 137-140, 142-145, 180, 184, 194, 212-225 |
| Ruthenium | 2, 4, 21, 34, 65, 66, 69, 71, 72, 76, 80, 207, 208   |
| Strontium | 2, 4-6, 8, 15-18, 21, 22, 30, 34, 42, 65-67, 69, 71, 72, 74-80, 83-92, 94-99, 101-111, 122, 126, 194, 198, 218, 226-228  |
| Tantalum  | 2, 4, 5, 21, 22, 34, 51, 65, 66, 69, 71, 72, 74-80, 122, 194, 195, 199, 200, 204-206, 229, 231   |
| Tellurium | 2, 4-6, 11, 21, 34, 55, 56, 65, 66, 69, 71, 72, 76, 78-80, 122   |
| Tin       | 2, 4-6, 10, 11, 18, 21, 22, 30, 33, 42, 65, 66, 68, 69, 71-80, 89, 90, 94, 99, 108, 120, 176, 184, 185, 232-235  |
| Tungsten  | 2, 4-6, 10, 11, 21, 22, 30, 33, 34, 47, 58, 65, 66, 69, 71, 72, 74-77, 79-81, 183-185, 191, 193, 236-239   |
| Uranium   | 2, 4, 6, 21-23, 30, 33, 34, 59, 61, 62, 65, 66, 71, 72, 74-80, 105, 232, 240-263   |
| Yttrium   | 2, 4-6, 8, 15-18, 21, 22, 30, 34, 42, 64-69, 71, 72, 74-80, 85-87, 89, 90, 96, 97, 99-102, 106-108, 110, 111, 122, 189, 194, 198, 264-269                                |
| Zirconium | 2, 4, 8, 15-17, 21, 22, 24, 30, 34, 40, 42, 65, 66, 71, 72, 74-80, 85, 87, 89, 94, 99, 101, 106, 107, 110, 111, 121-125, 127, 129-131, 134                               |

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